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CHEMICAL IDENTIFICATION OF THE ODOR COMPONENTS IN DIESEL ENGINE EXHAUST

Final Report (Year 2) to

COORDINATING RESEARCH COUNCIL

and

NATIONAL AIR POLLUTION CONTROL ADMINISTRATION
U. S. PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

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Arthur D. Little, Inc.

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June 1970

Arthur D. Little, Inc.

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I. SUMMARY

A. INTRODUCTION

This report concludes the second year of a research program to chemically identify the odor components of diesel exhaust. The study is sponsored jointly by the Coordinating Research Council and the National Air Pollution Control Administration, U.S. Public Health Service, as part of their continuing support of programs designed to obtain a detailed technical understanding of diesel exhaust and its odor.

During the first year of the program, we developed an experimental approach[1] which involved sensory characterization as an integral part of the study. We also developed methods for collecting large volumes of diesel engine exhaust by condensation at 0°C, extracting the organic portion of the exhaust condensate, and separating the odorous components of the extract from the non-odorous (and major) portion by liquid chromatography. The odorous species separated into two major odor fractions with roughly equal odor intensities – oily-kerosene and smoky-burnt. At the completion of the first year's study we were developing methods for resolving both of these odor fractions into single species for odor description and chemical identification. A two-stage gas chromatography (GC) approach demonstrated promise for the final resolution.

B. RESULTS

In this second year of the program we have refined the two-stage gas chromatographic method for resolution of the odor fractions using an efficient GC fraction trapping method and applied it with great success to the oily-kerosene odor fraction obtained from the first-stage, liquid-column chromatography (LCC) separation. The odors of the individually resolved compounds were characterized and their structure determined by high resolution mass spectrometry. The overall approach is shown schematically in Figure 1.

Using this approach, together with quantitative odor studies on selected reference components, we have been able to determine the chemical structure of the principal components responsible for the characteristic oily-kerosene portion of diesel exhaust odor. The chemical classes associated with the odor in this complex are:

alkyl benzenes,
indans/tetralins, and
indenes.

1. Chemical Identification of the Odor Components in Diesel Engine Exhaust, final report July 1969, CRC Project CAPE-7-68, HEW CONTRACT PH 22-68-20.

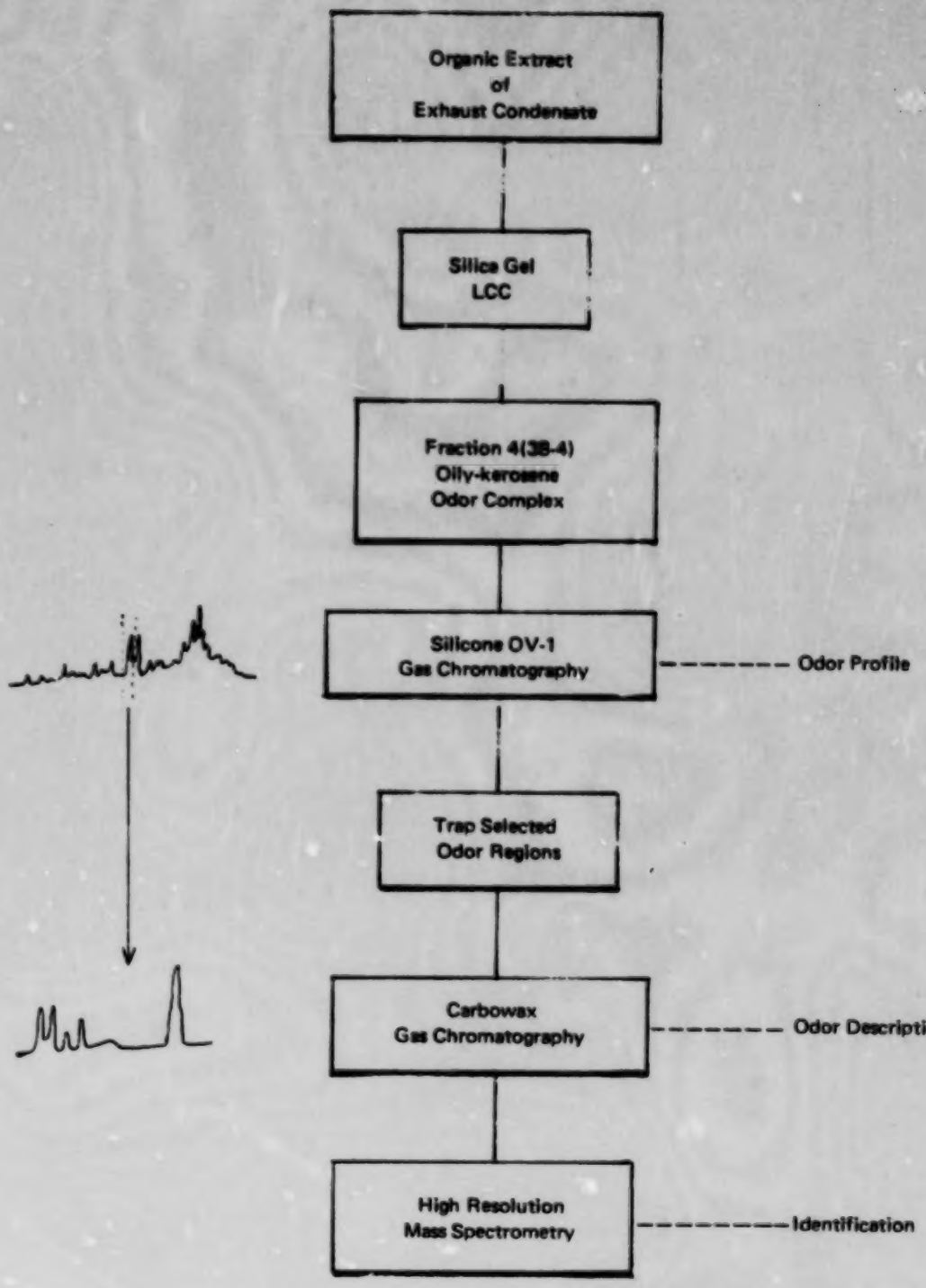


FIGURE 1 IDENTIFICATION SEQUENCE FOR OILY-KEROSENE ODOR COMPLEX

from page 1

Alkyl naphthalenes constitute a major portion of the mass of the oily-kerosene fraction but are not a direct major odor contributor. However, they may make some overall contribution to the odor perception through a synergistic effect.

Detailed comparison studies of comparable oily-kerosene odor fractions from the diesel engine exhaust and the original fuel indicate that they are similar chemically. It is very likely, therefore, that the unburned fuel contributes heavily to the oily-kerosene odor note.

Some limited success was achieved in applying the techniques described above to the smoky-burnt odor fraction and several individual odor species were identified. The LCC and GC separation steps used for oily-kerosene fractions did not provide sufficient resolution for successful application of mass spectrometry to this sample. Therefore, we explored several alternative means for obtaining greater resolution of the smoky-burnt odor complex. The approach finally derived was a modification of the scheme shown in Figure 1. For identification of the smoky-burnt odor complex, only the chloroform extract from the initial exhaust condensate is submitted to LCC (both the pentane and chloroform extracts were used for the oily-kerosene odor complex) and the LCC step itself employs a finer gradient elution on a micro-column scale.

This latter scheme has enabled us to obtain smoky-burnt odor fractions from the micro LCC which exhibit sufficient resolution in the first silicone chromatogram to apply the mass spectrometric methods used in the oily-kerosene complex for this fraction. Some preliminary identification studies have been carried out on incompletely resolved regions of odor importance eluting from the silicone GC column. The major chemical classes observed in the regions of odor interest are the alkyl derivatives of species such as furfural, xylenol, benzofurfural, dienones, phenyl propenic acids, and phenyl carbonyls. Detailed odor and chemical structure assignments for this odor fraction await the application of the two-stage GC approach for the study of resolved single species.

C. RECOMMENDATIONS

1. The improved resolution techniques that we have developed should be applied to the smoky-burnt odor complex in an effort to determine its chemical nature.

2. Once the odor-structure identification studies are complete, studies should be initiated to determine the influence of engine operating variables and fuel types on diesel exhaust odor. In these initial studies the method should be essentially the same as our present research methodology for measurement of the odor species.

3. Studies should be undertaken to develop simpler methodology for the measurement of odor species. The goal of such simplification should be an instrumental method which could be used in the many laboratories conducting research on the diesel exhaust odor problem.

II. BACKGROUND

This section briefly reviews the approach developed during the first year of our research program.

Our success has resulted from an approach which combines the sensory talents of odor chemists with the capabilities of analytical chemists to produce a working scheme for separating the odor components from the bulk of diesel engine exhaust.

The engine used in these studies is a 71-series 4-cylinder diesel* that has been operated under constant conditions of 1800 rpm and 30% load from a single large fuel supply. The exhaust from the engine can be passed into an adjacent aluminum-lined odor test room for sensory evaluation or through a sampling system for collection and analysis. A typical odor description using the ADL odor profile method (see Appendix A) is:

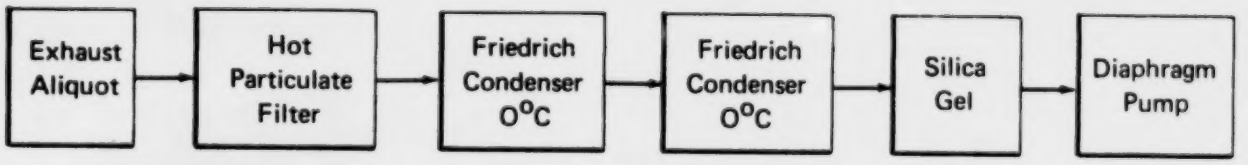
TIA 2

oily	2
burnt	2
kerosene	1½
eye irritation	√
nose irritation	√

(600/1 dilution: 21 ℓ of exhaust in 12,500ℓ test room) .

Thus, in terms of the overall perception of diesel exhaust odor, the odor quality and intensity is comprised about equally of an oily-kerosene and a smoky-burnt odor complex.

Our preferred approach for collection of the odor sample is:



Large volumes of the exhaust sample are passed through unheated 1/2-inch stainless steel pipe, a heated fiber glass filter, and two Friedrich condensers (kept at 0° C) in series. All condensate is collected in round-bottom flasks and kept at

*Detroit Diesel Division of General Motors Corporation, Model 4154N.

0° C. The remaining gases are swept through a silica-gel column, roughly 2-inch OD and 2-10 inches high.

At flow rates of 0.5-1.0 cfm (15-30 ℓ/min), we are able to collect about 1000 ℓ/hr and usually accumulate 20,000-60,000 liters of exhaust condensate for the generation of analytical samples.

The standard basic sample workup procedure which we developed during the program is shown in Figure 2. The oil phase which separates from large volumes of exhaust condensate is combined with the pentane and chloroform extracts to provide the concentrated organic portion of the diesel exhaust. This organic concentrate is first separated into major fractions by silica-gel, liquid-column chromatography (LCC) yielding a major non-odorous fraction (SiO_2-1) and two major odorous fractions – oily-kerosene (fraction SiO_2-4) and smoky-burnt (fraction SiO_2-10) (see Appendix B for details of the LCC step.) Other non-odorous species in these fractions are separated, and the remaining odorous species are resolved into individual chemical species by two stages of gas chromatography (GC). The first stage uses a silicone column and the second a carbowax column. The chemical structure of odorous compounds is identified by high resolution mass spectrometry (HRMS).

Throughout the program, we have depended on the odor profile technique to determine whether samples of diesel exhaust maintained their odor character after each purification step.

As described in greater detail in Section III B, the method finally found acceptable for the smoky-burnt odor complex represents an improved modification of this basic scheme.

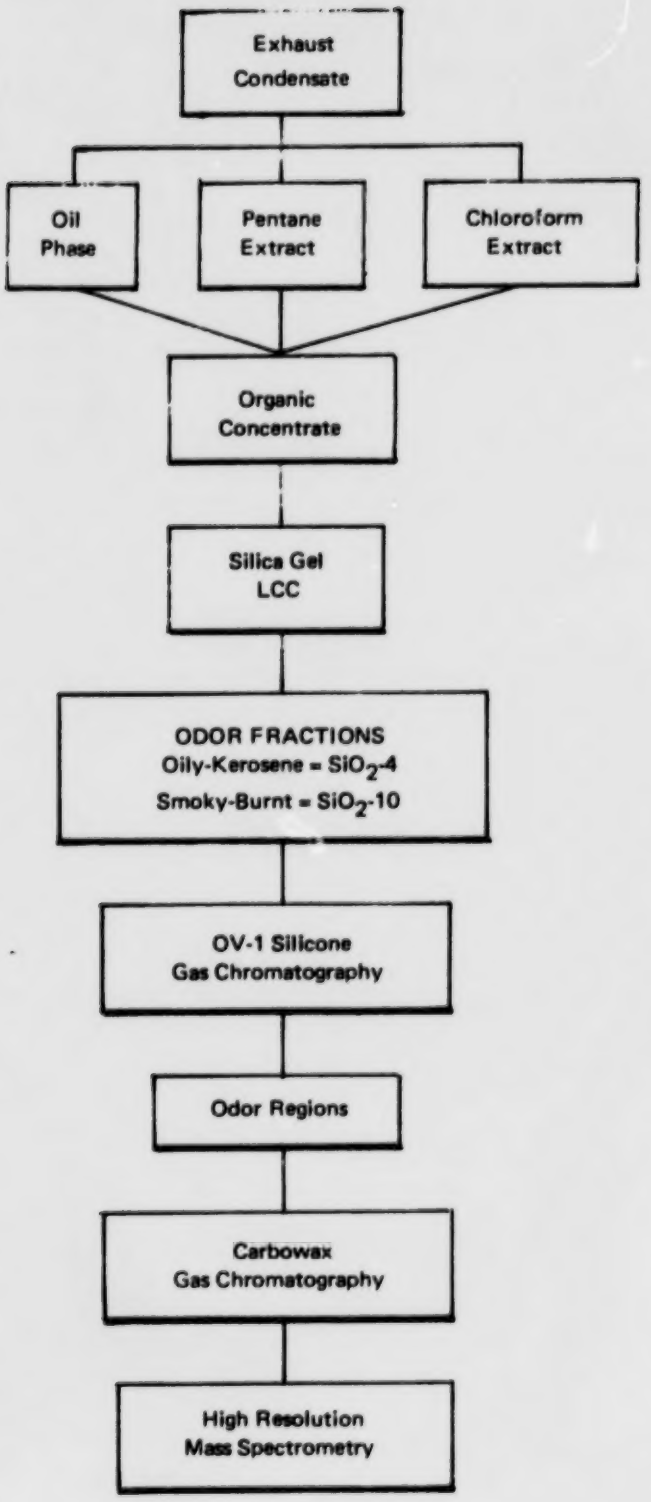


FIGURE 2 STANDARD DIESEL EXHAUST WORKUP PROCEDURE

III. IDENTIFICATION AND CHARACTERIZATION OF ODOR COMPONENTS

A. OILY-KEROSENE ODOR COMPLEX

1. Chemical Identification of Odor Compounds

We have applied the basic separation scheme shown in Figures 1 and 2 to identify the oily-kerosene odor components present in the SiO_2-4 fraction from the liquid-column chromatographic (LCC) separation step. The techniques employed to transfer the regions of odor interest from the silicone GC column to the Carbowax GC column are described in Appendix C.

Figure 3 is the gas chromatogram of the oily-kerosene odor fraction on the silicone column. This sample, 38-4, is from Experiment 38. From an examination of the fraction's odor profile, we chose the areas indicated in Figure 3 as relevant to the oily-kerosene odor complex and designated these areas for collection and further resolution. Two aliquots of each area were collected for resolution on the Carbowax GC column. The first sample was used to obtain the gas chromatogram and the odor profile. The second sample was used to record high-resolution mass spectra (HRMS) of those peaks whose odor pertained to the oily-kerosene odor complex.

Figure 4 shows the results obtained on silicone peak 3 of the 38-4 exhaust fraction. Each peak of odor interest in the Carbowax chromatograms was assigned a number in addition to the original silicone column peak numbers (Figure 3). Thus, each compound has a unique identification such as 38-4-4-2 representing: (Experiment 38)–(oily-kerosene LCC fraction 4)–(silicone peak 4)–(Carbowax peak 2). For our purposes in this report, it is sufficient to refer to the last two GC peak numbers, e.g., 4-2. The approximate percentage of the total 38-4 fraction which each of the peaks represents is also indicated. The percentage is a first approximation based on measurement of relative peak heights in the two sets of chromatograms. The structure and odor of each of the compounds are also described.

Similar data were obtained on 12 other peaks in the silicone chromatogram. (See Appendix D.) Each of the compounds of odor interest in the Carbowax chromatogram was identified by high-resolution mass spectrometry (Appendix E). With only two exceptions, every compound was identified by asking the computer to search only for combinations of C, H, and O. No oxygenates were found. With a second analysis, allowing a search for combinations of C, H, N, O, and S, two previously unidentified compounds were identified as benzothiophenes. (Silicone peaks 17 and 19.) No other heterocyclic possibilities were identified. Except for the two benzothiophenes, all of the compounds were hydrocarbons.

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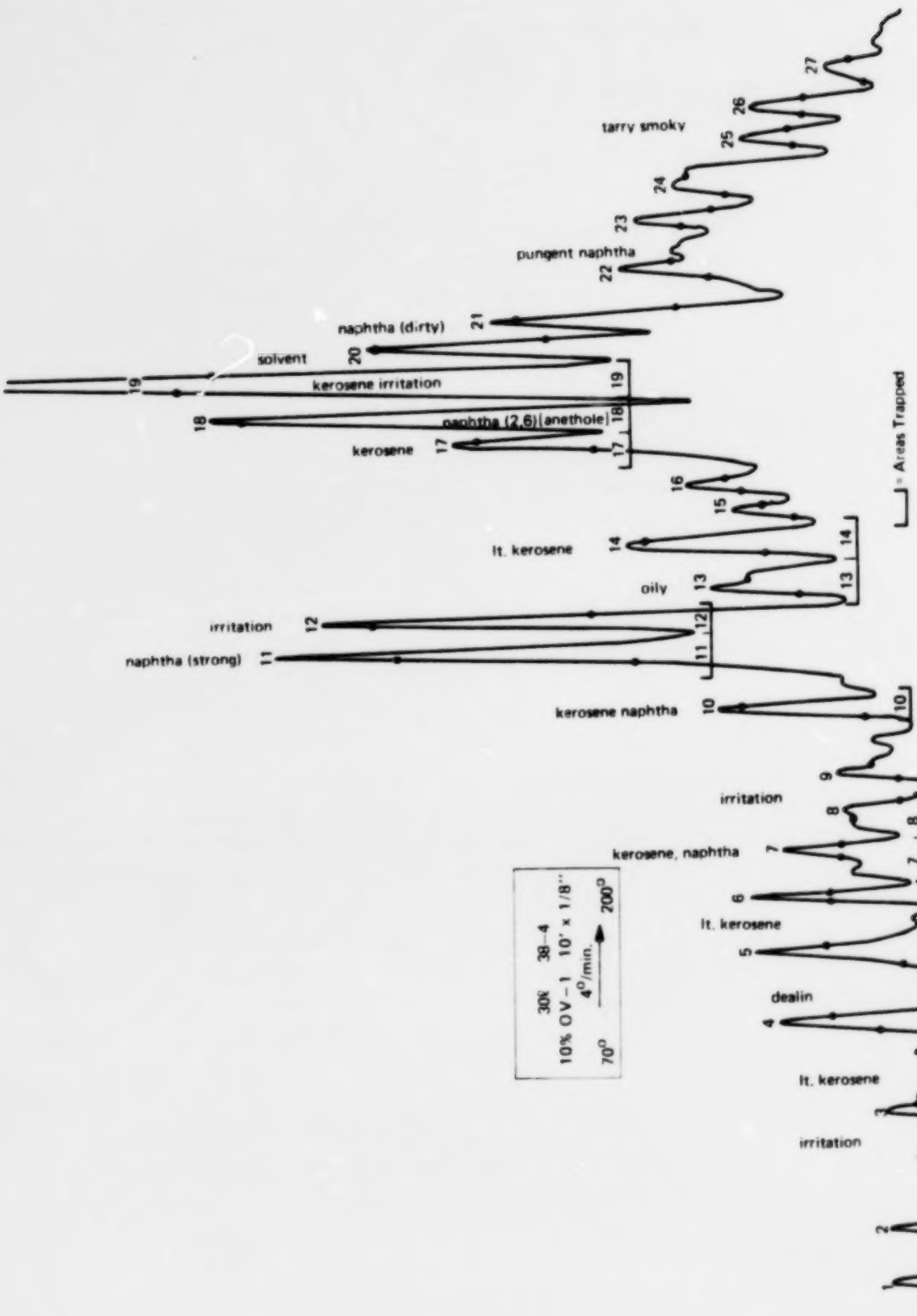
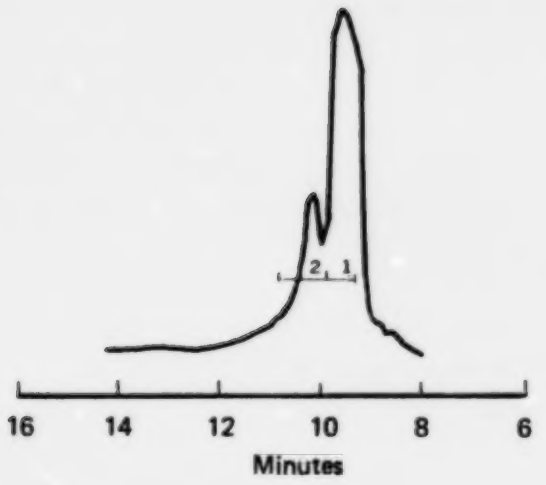


FIGURE 3 SILICONE GAS CHROMATOGRAM OF 38–4 OILY–KEROSENE EXHAUST FRACTION



Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min.

CBW	%[a]	MW	Composition	Odor
1	1	134	$C_{10}H_{14}$ alkyl benzene	rubbery
2	0.2	132	$C_{10}H_{12}$ methylindan	irritation

a. Approximate percentage of total 38-4 fraction.

FIGURE 4 SILICONE PEAK 3 ON CARBOWAX

Our work does not preclude the possibility, however, that other heterocyclic species are present in the samples below the detectability limit.

The elemental composition determined from the high-resolution mass data allows one to restrict the possible chemical structural choices for a particular compound to relatively few. In addition, the fragmentation patterns allow one to readily distinguish between choices such as an aromatic compound and an acyclic polyolefin. As a further aid in identification, we utilized our earlier observation that the oily-kerosene fraction represents a portion of the unburned fuel and concluded that it was reasonable to look for those structure types normally found in petroleum distillates.

Using information derived from all of the sources described above, we have identified the following structure classes in the 38-4 fraction:

indans
tetralins
alkyl benzenes
naphthalenes
indenes
acenaphthenes
benzothiophenes

Some attempt has also been made to refine the assignments for individual species to more specific structures. At present we have used only the mass spectral fragmentation data in arriving at tentative isomer assignments (Appendix E).

These data are summarized in Tables 1-4 by structure class. The compounds listed in these tables account for about 50% of the 38-4 fraction. By comparing the gas chromatographic retention times with the mass spectral data, we can say that most of the data in Tables 1-4 represent distinctly different compounds. The variation in isomers of the same elemental composition is probably due to branching and positional location of alkyl groups. The isomeric structures very likely account for the different odors associated with the same elemental composition (but different specific compound).

All of the kerosene related odor notes were perceived in connection with the indans and tetralins which represent about 12% of the sample. Twenty-one distinct indans and tetralins were observed – two $C_{10}H_{12}$, three $C_{11}H_{14}$, eleven $C_{12}H_{14}$ and five $C_{12}H_{18}$ isomers (Table 1). Odor pertaining to the perception of kerosene was associated with 11 of these compounds. Several of the compounds were perceived as irritating and may influence the overall perception of the exhaust odor. The one case of a sulfide odor is associated with tetralin, which normally has an odor related to kerosene. It is possible that sulfur compounds are

TABLE 1

SUMMARY FOR INDAN AND TETRALIN COMPOUNDS

Peak[a]	Percent[b]	MW	Elemental Composition	Compound	Odor
3-2	0.2	132	$C_{10}H_{12}$	methyl indan	irritation
5/6-3	0.2	132	$C_{10}H_{12}$	tetralin	rubbery sulfide
7-1	0.05	160	$C_{12}H_{16}$	dimethyl tetralin	kerosene[c]
7-3	0.1	146	$C_{11}H_{14}$	dimethyl indan	kerosene[c]
8-2	0.3	160	$C_{12}H_{16}$		indole like
10-2	2	146	$C_{11}H_{14}$	methyl tetralin	naphthenate[c]
11-1	0.1	174	$C_{13}H_{18}$	trimethyl tetralin	naphthenate[c]
11-2	0.5	160	$C_{12}H_{16}$	dimethyl tetralin	–
11-3	0.5	160	$C_{12}H_{16}$	trimethyl indan	kerosene[c]
11-6	1	146	$C_{11}H_{14}$	methyl tetralin	naphthenate[c]
12-1	0.5	174	$C_{13}H_{18}$	alkyl tetralin	irritation
12-2	1	160	$C_{12}H_{16}$		irritation
13-3	1	160	$C_{12}H_{16}$		–
14-2	3	174	$C_{13}H_{18}$		kerosene[c]
		160	$C_{12}H_{16}$		related
14-3	0.2	160	$C_{12}H_{16}$	dimethyl tetralin	kerosene[c]
17-1	0.1	160	$C_{12}H_{16}$	alkyl tetralin	solvent (kerosene)[c]
18-1	0.1	174	$C_{13}H_{18}$		pungent, acrid
18-2	0.1	160	$C_{12}H_{16}$		kerosene[c]
19-1	1	174	$C_{13}H_{18}$		light
	—	160	$C_{12}H_{16}$		kerosene[c]
	12% Total				

a. Peak from the silicone (1st digit) and Carbowax (2nd digit) GC columns.

b. Approximate percentage of total 38-4 exhaust fraction.

c. Kerosene related odor notes.

TABLE 2

SUMMARY FOR ALKYL BENZENE COMPOUNDS

Peak[a]	Percent[b]	MW	Composition	Odor
3-1	1	134	$C_{10}H_{14}$	rubbery
4-2	2	134	$C_{10}H_{14}$	musty oily[c]
5/6-1	0.2	148	$C_{11}H_{16}$	strong
5/6-2	0.2	134	$C_{10}H_{14}$	tarry
7-1a	0.05	162	$C_{12}H_{18}$	wax[c]
7-2	1	148	$C_{11}H_{16}$	–
8-1	0.1	162	$C_{12}H_{18}$	irritation
8-3	0.3	148	$C_{11}H_{16}$	oily metallic[c]
8-4	0.3	148	$C_{11}H_{16}$	oily[c]
10-1	0.2	162	$C_{12}H_{18}$	rubbery (not sulfur)
11-1	1	162	$C_{12}H_{18}$	–
11-4	1	148	$C_{11}H_{16}$	–
14-1	0.2	uncertain[d]		oily[c]
	8%			

a. Peak from the silicone (1st digit) and Carbowax (2nd digit) GC columns.

b. Approximate percentage of total 38-4 exhaust fraction.

c. Oily related odor notes

d. MW uncertain, but fragmentation pattern determines structure type.

TABLE 3

SUMMARY FOR NAPHTHALENE COMPOUNDS

Peak[a]	%[b]	MW	Elemental Composition	Compound	Odor
11-7	4	142	$C_{11}H_{10}$	monomethyl	feel (mothballs)
12-4	2	142	$C_{11}H_{10}$	monomethyl	irritation
17-2	5	156	$C_{12}H_{12}$	dimethyl	none
18-3	7	156	$C_{12}H_{12}$	dimethyl	none
18-2	12	156	$C_{12}H_{12}$	dimethyl	none
	30%				

a. Peak from the silicone (1st digit) and Carbowax (2nd digit) GC columns.

b. Approximate percentage of total 38-4 exhaust fraction.

TABLE 4

SUMMARY OF INDENE, ACENAPHTHENE, AND BENZOTHIOPHENE COMPOUNDS

Peak[a]	%[b]	MW	Elemental Composition	Compound	Odor
13-3	0.1	172	$C_{13}H_{16}$	alkyl indene	heavy oil
13-4	0.05	158	$C_{12}H_{14}$	alkyl indene	heavy oil
17-2	0.01	162	$C_{10}H_{10}S$	dimethylbenzothiophene	none
19-2	0.01	162	$C_{10}H_{10}S$	dimethylbenzothiophene	none
19-2	0.5	168	$C_{13}H_{12}$	acenaphthene	none
	0.7%				

a. Peak from the silicone (1st digit) and Carbowax (2nd digit) GC columns.

b. Approximate percentage of total 38-4 exhaust fraction.

present in cases where a sulfide odor is perceived, but their odor threshold is so much lower than the hydrocarbons that we would not be able to detect them.

The oily-related odor notes seem to be associated primarily with the alkyl benzenes (Table 2), although the alkyl indenes (Table 4) seem to be an important contributor to the oily odor complex. The alkyl benzenes account for 8% of the sample with three $C_{10}H_{14}$, five $C_{11}H_{16}$, and four $C_{12}H_{18}$ isomers.

The major portion (30%) of the 38-4 sample is represented by the alkyl naphthalenes (Table 3), but they do not contribute any of the oily-kerosene odor notes. Irritation from monomethyl naphthalenes may contribute slightly to perception of the odor complex, however.

Data for the acenaphthene and benzothiophenes are given in Table 4. These were observed at a trace level in the samples and eluted at the same time as the dimethylnaphthalenes where no odor was perceived.

The overall correlation derived from these studies is presented in summary form in Table 5. We may be able to refine our odor-structure correlation as reference compounds become available.

2. Estimated Concentration of Oily-Kerosene Odor Components in Diesel Exhaust

From the data obtained from the GC response for odorous compounds, we have estimated the concentration of the oily-kerosene odor species (Table 6). Calculations are given for both the total group of compounds associated with the oily-kerosene odor and for individual odor species. The concentration calculated for the total odor complex in the exhaust is in accord with the odor thresholds expected for the species which we have identified and is consistent with the results obtained for the reference compounds reported in Section III-A4.

3. Potential Source of Oily-Kerosene Odor Compounds

Earlier chromatographic and odor characterization studies indicated that the oily-kerosene portion of diesel exhaust odor was similar to that found in the fuel. We have carried out several detailed studies to examine this relationship in greater detail.

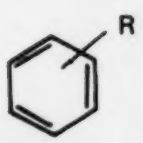
a. Chromatography and Odor Comparison

A sample of No. 1 diesel fuel was subjected to the standard silica gel liquid chromatographic separation scheme used for the first-stage separation of the exhaust samples. The first two benzene fractions (FO-4 and FO-5), which

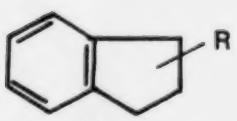
TABLE 5

ODOR-STRUCTURE CORRELATION FOR THE OILY-KEROSENE ODOR COMPLEX

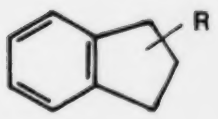
Odor Type	Associated Structures
Oily	alkyl benzenes[1] alkyl indenes[2]
Kerosene	alkyl indans[3] alkyl tetralins[4]
Sensation (feel, irritation)	methyl naphthalenes[5]



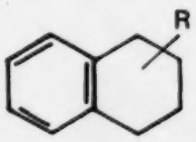
(1)



(2)



(3)



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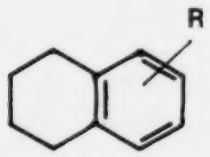

(5)

TABLE 6

ESTIMATED CONCENTRATIONS OF OILY-KEROSENE ODOR COMPLEX

Fraction	Fraction Weight (μg)[a]	Percent of Previous Fraction	Concentration of	
			Total O-K Fraction[b]	Individual O-K Components[c]
Exhaust	0.7×10^9	–	3 ppm	6-60 ppb
Condensate	20×10^6	3	100 ppm	0.2-1 ppm
Organic Extract	100×10^3	0.5	2%	20-200 ppm
Total Fraction 4	10×10^3	10	20%	0.02-0.2%
Total O-K Odor Components	2×10^3	20	–	0.1-1%
Individual O-K Species	10 - 100	0.1 - 1		–

a. For 1000 liters of diesel exhaust.

b. Concentration of total components pertaining to oily-kerosene odor.

c. Concentration of individual oily-kerosene odor species.

contained the oily-kerosene related odor notes, were compared with the oily-kerosene fraction (38-4) obtained by chromatographic separation of the condensate extract from 20,000 liters of diesel exhaust. A flow diagram of the experimental preparation for these samples is shown schematically in Figure 5. The results of evaluating these fractions in the odor test room are given in Table 7.

The odor evaluation of the SiO_2-4 fractions from the two sources was quite similar, with the difference that the oxidized oily note was perceived first in the exhaust sample. The gas chromatogram of FO-4 on the OV-1 silicone column is shown in Figure 6 and should be compared to Figure 3, the chromatogram of 38-4. Except for the higher intensity of low-boiling components in FO-4, the chromatograms are virtually identical on a peak comparison basis. The similarity of the fuel oil and exhaust derived samples is quite striking.

b. Chemical Identification

To further examine the possibility that the oily-kerosene odor species in the exhaust are also present in the fuel, we carried out two studies by mass spectrometry: (1) HRMS studies on fuel oil-4 fractions eluting from the silicone GC column and (2) matrix comparison studies on exhaust and fuel fractions.

In our initial identification work we could not make chemical assignments until we had first isolated the odor species by a two-stage gas chromatography (GC) approach using silicone and Carbowax columns on the LCC-4 fraction from exhaust. However, once we knew which compounds were important from an odor point of view, it was not necessary to purify the fractions so thoroughly before we undertook qualitative analysis. Therefore, we were able to determine whether they are present in the fuel by using a standard liquid-column chromatographic procedure (Fraction 4) followed by a single silicone GC separation and high-resolution mass spectrometry. The HRMS provides the extra resolution required to differentiate the various chemical classes still present in narrow elution regions from the silicone GC.

On the basis of odor compounds we knew to be present in particular regions (peaks) in the exhaust fraction, we examined these same regions (peaks) in the fuel fraction by combined GC/HRMS. We then examined the HRMS data to determine whether the odor species found in the exhaust could also be observed in the fuel.

Upon examination of the HRMS computer printouts, we concluded that each of the odor species found in the exhaust fraction is also found in the fuel. In many instances, these species (alkyl benzenes, indans, tetralins, indenes, naphthalenes) are a major portion of the GC peak. Many other species were also observed in the spectra, but we are not certain of their contribution to the oily-kerosene odor.

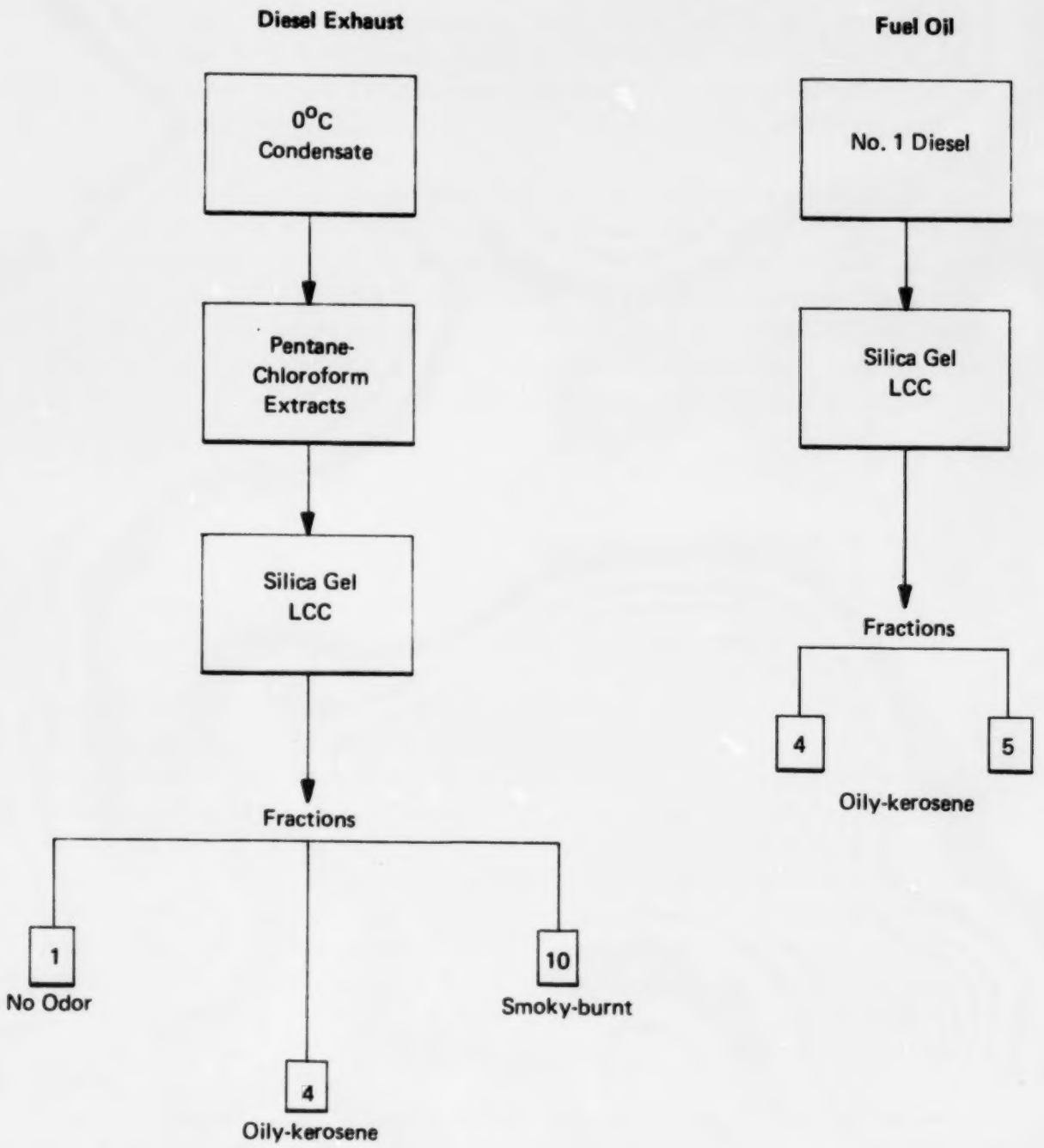

FIGURE 5 SOURCE ORIGIN OF OILY-KEROSENE ODOR SAMPLES

TABLE 7

ODOR DESCRIPTION OF FRACTIONS DERIVED FROM FUEL OIL AND DIESEL EXHAUST

SiO_2 Fraction	Fuel Oil (37 $\mu\ell$)		Exhaust (210 ℓ)	
	Code	Odor	Code	Odor
4	FO-4	TIA 1½ kerosene sour 1½ oxidized oily ½-1 burnt)(eye irritation nose irritation	38-4	TIA 1-1½ oxidized oily 1-1½ kerosene sour 1 rubbery? eye irritation nose irritation
5	FO-5	TIA 1½-2 kerosene (fly spray) 1½ oxidized oily 1½ eye irritation nose irritation	38-5	TIA ½ oxidized oily)(-½ sour ½

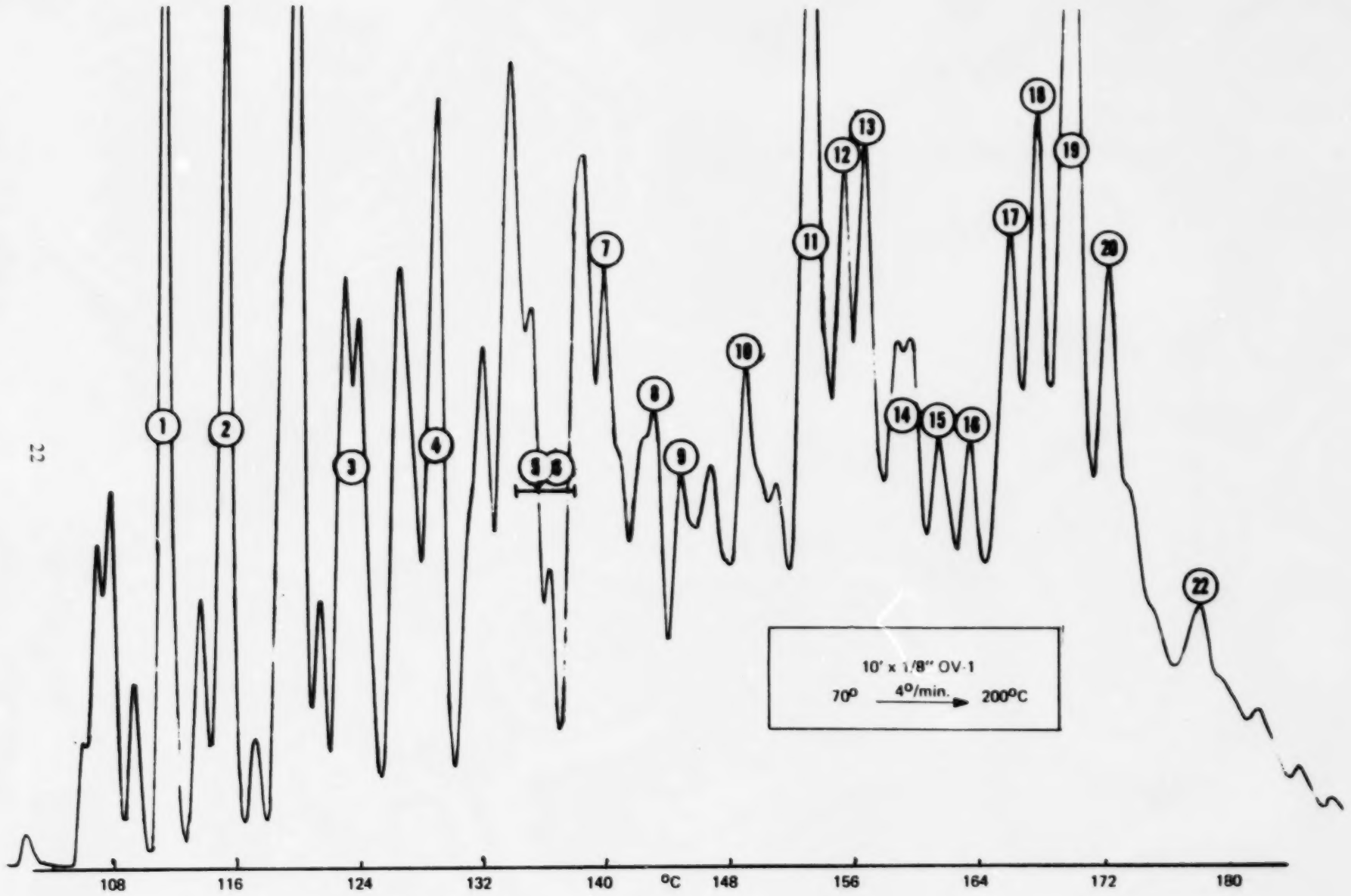

FIGURE 6 SLOW GC PROGRAM OF FUEL (FO-4) OILY-KEROSENE FRACTION

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Oily kerosene samples from an exhaust fraction (42-4) and fuel (FO-4) were sent to Mobil Research and Development Corporation in Paulsboro, N.J., for a mass spectrometric comparison using their standard matrix analysis for high molecular weight hydrocarbons. The test is similar to ASTM D2425-67.

The results from these analyses are summarized in Table 8. It is interesting that the species we would expect to be more easily oxidized, such as the alkyl benzenes, are lower in concentration in the exhaust fraction than in the fuel. The relative distribution by carbon number (molecular weight) for each of the classes is given in Figures 7 and 8. The intensity in each class for each fraction has been normalized to 100 in order to see more clearly whether there has been any specific shift in a particular chemical class. It appears that the lower molecular weight compounds are generally less abundant in the exhaust than in the fuel and that the combustion process has not caused any specific shift in composition by chemical class.

4. Odor Confirmation of Oily-Kerosene Compounds

To determine the validity of the odor-structure assignments determined from the GC/HRMS data, we carried out odor studies on several reference compounds available for examination.

Several alkyl benzenes, indans, and tetralins were obtained for odor studies through the courtesy of the Mobil Research and Development Corporation. The compounds were selected on the basis of chemical classes identified as being important in the oily-kerosene odor complex and probable availability as determined by the API standards list.

The compounds obtained for study are listed in Table 9 along with our working code. The qualitative odor description given in the table was obtained for each of the compounds by directly smelling a vial containing the sample and from blotter strip evaluation. From the initial odor screening, we selected five compounds for further study in the odor test room. The five were selected on the basis of their similarity to diesel exhaust characteristics and their relatively high odors. The individual compounds were studied by injecting several concentrations into the odor test room, including levels estimated to be present in diesel exhaust. The results obtained with these compounds are given in Table 10. From our previous work (see Table 6) we estimated that the compounds contributing to the oily-kerosene odor complex are present in diesel exhaust at about 1 ppm (V/V). Compounds OK 2, 4, 12 and 14 have odor intensities at the 1-3 ppm level, quite consistent with the odor intensity of diesel exhaust itself. Compounds OK 7, 10 and 16 had higher odor thresholds as indicated by the increased concentration required to obtain measurable odors.

TABLE 8

ANALYSIS OF HIGH-MOLECULAR WEIGHT AROMATICS

Component	Oily-Kerosene Fraction From	
	Fuel (FO-4)[a]	Exhaust (42-4)[a]
Alkyl benzenes	68.4	23.7
Tetralins, Indans, Indenes	18.7	38.7
Alkyl naphthalenes	12.9	37.6
Odor Characterization of Fractions		
	TIA 1½ kerosene oily 1½ oxidized oily ½-1 burnt)(eye irritation nose irritation	TIA 1-1½ oxidized oily 1-1½ kerosene sour 1 rubbery? eye irritation nose irritation

a. Mole %

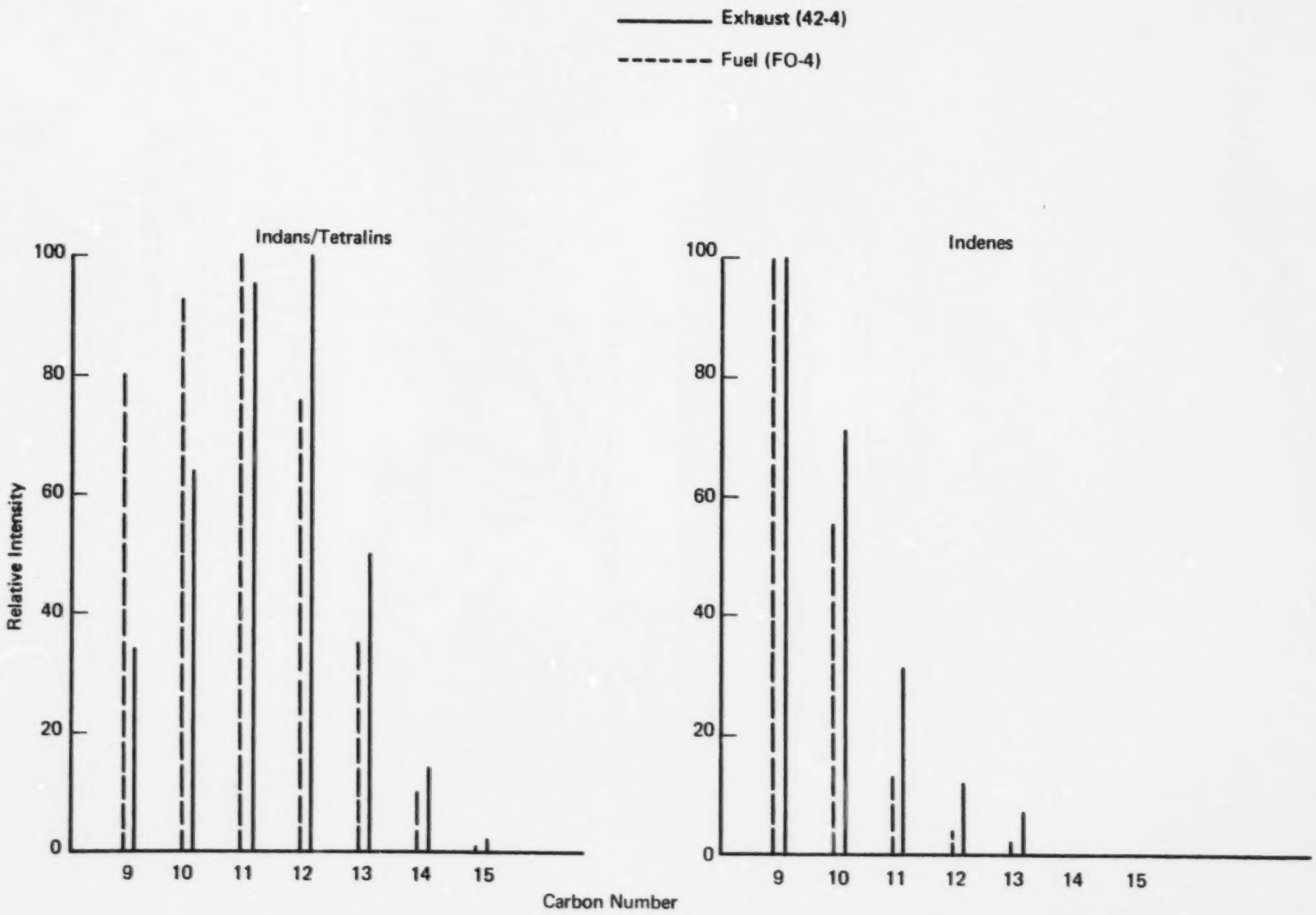

FIGURE 7 RELATIVE DISTRIBUTION OF INDANS/TETRALINS AND INDENES

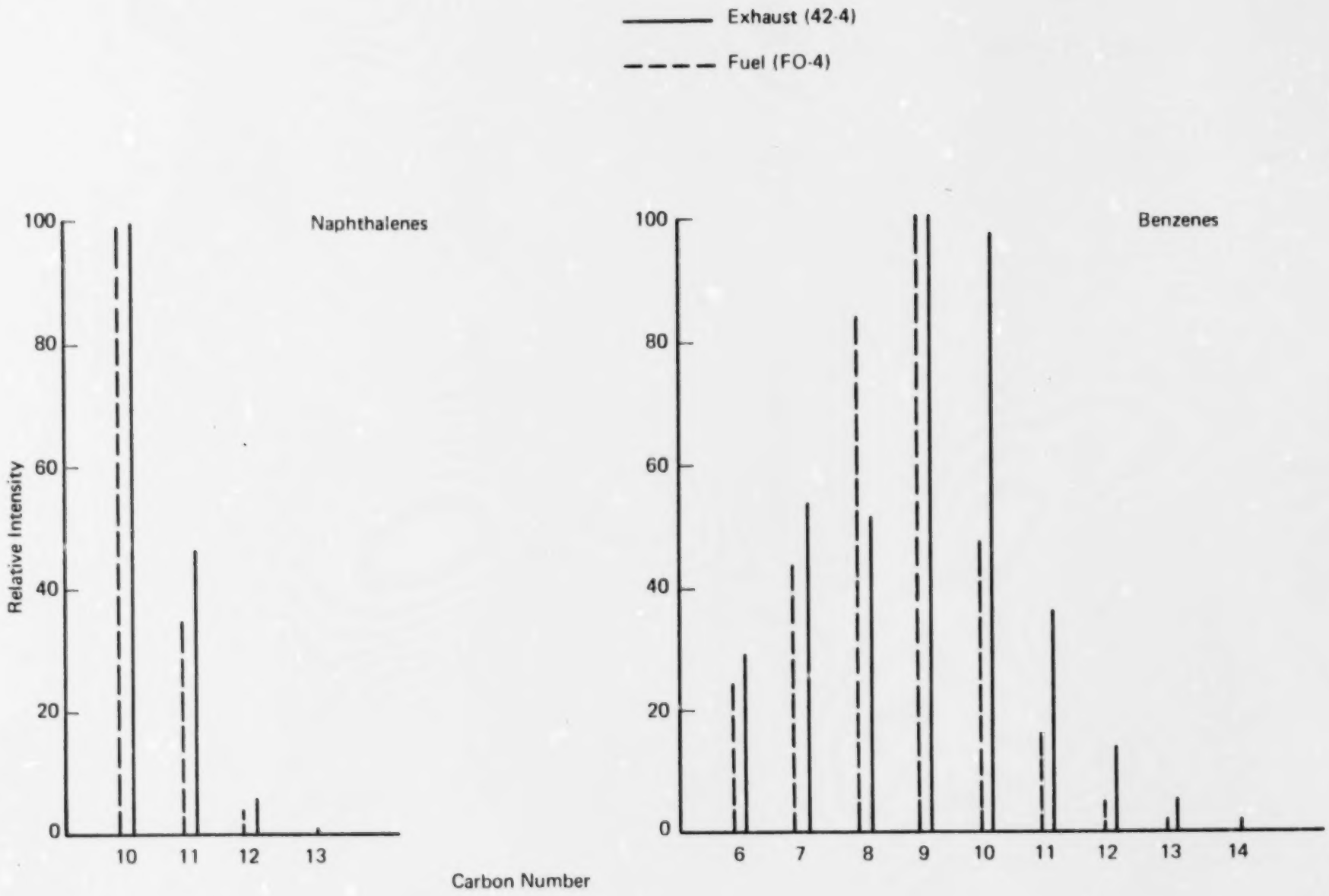

FIGURE 8 RELATIVE DISTRIBUTION OF NAPHTHALENES AND BENZENES

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TABLE 9

OILY-KEROSENE REFERENCE COMPOUNDS

Code	Sample	Qualitative Odor Description
OK 1	1,3-Diethylbenzene (99.8%)	Naphtha, musty estery
OK 2	1,4-Diethylbenzene (99%)	Oily, sour, anise
OK 3	1-Methyl-2-Ethylbenzene (99.7%)	Sweet (ionone) oily
OK 4	1-Methyl-3-n-Propylbenzene (99.7%)	Solvent, pungent, estery
OK 5	1-Methyl-3-iso-Propylbenzene (99.8%)	Oily, pungent, naphtha
OK 6	1-Methyl-4-n-Propylbenzene (99.6%)	Oily, sour, cumene
OK 7	1-Methyl-4-iso-Propylbenzene (99.8%)	Sour, pungent, cumene
OK 8	1,3-Dimethyl-5-Ethylbenzene (99.7%)	Green, sour oily
OK 9	1,2,3-Trimethylbenzene (99.5%)	Green, pungent, sour
OK 10	1,2,4-Trimethylbenzene (99.6%)	Pungent, sour, camphor
OK 11	1,3,5-Trimethylbenzene (99.8%)	Pungent, sour
OK 12	1,1-Dimethylindan	Oily, metallic, solvent
OK 13	1,1,4,6-Tetramethylindan	Pungent, oily, sour
OK 14	2,6-Dimethyltetralin	Oily, sour, linseed
OK 15	2,5,8-Trimethyltetralin	Sweet, metallic, rubber
OK 16	2,2,5,7-Tetramethyltetralin	Solvent (fly spray), pungent

TABLE 10

REFERENCE COMPOUND QUANTITATIVE ODOR EVALUATION

Code	Compound	Test Room Odorant Conc. µg/ℓ	Test Room Odorant Conc. ppm (V/V)	TIA	Character
OK 2	1,4-diethylbenzene	0.02	3	1½	sour-anethole like
OK 4	1-methyl-3-n-propylbenzene	0.01	1	1	sour, pungent, fruity
OK7	1-methyl-4-isopropylbenzene	0.3	40	½	oily
OK 10	1,2,4-trimethylbenzene	0.4	50	½	sour
OK 12	1,1-dimethylindan	0.02	3	1	sour, leathery
OK 14	2,6-dimethyltetralin	0.02	3	) (	oily?
OK 16	2,2,5,7-tetramethyltetralin	0.08	12	1	flyspray, solvent

Several mixtures of the compounds produced an odorant blend similar in character to the fuel. These limited studies verify that the chemical structures assigned to particular odor classes for the oily-kerosene portion of diesel exhaust are substantially correct.

B. SMOKY-BURNT ODOR COMPLEX

1. Initial Progress on the Identification of Resolved Components

At the end of the first year's program we had arrived at the point where some limited success was obtained in the resolution of individual compounds in the smoky-burnt odor complex isolated in the SiO_2-10 LCC fraction. Using a two-stage GC technique which was not as refined as our present methodology, we were able to resolve compounds eluting in the early portion of the silicone GC chromatogram. Some limited identification studies were carried out using this approach – which is basically the approach used successfully for the oily-kerosene odor complex.

A standard SiO_2-10 smoky-burnt fraction was prepared from a 76,000-liter, diesel-exhaust trapping in Experiment 25. After suitable concentration of this fraction, its odor profile was determined on the OV-1 silicone GC column. The concentrated SiO_2-10 sample was designated 29A. The GC results using a 10°C/min program rate (in the later oily-kerosene studies the rate was 4° /min) are shown in Figure 9. Fractions I, II, and III were successfully trapped during the silicone elution and further resolved on the Carbowax GC column (Figures 10-12). High-resolution mass spectra were obtained on the peaks in the chromatograms indicated by the peak numbers. A summary of the odor and chemical structure data obtained for these peaks is given in Table 11. The structures indicated in the table are tentative assignments in some cases.

From these data it appears that the phenols contribute to the irritation factor associated with diesel exhaust. Many of the burnt odors in this series of experiments were associated with furfural derivatives.

As explained in our last final report, we were unable to apply this approach to the rest of the region eluting from the silicone GC, because the higher boiling fractions were still much too complex to be resolved on the Carbowax column. It is evident even in the data in Table 11 that some of the peaks were still unresolved mixtures.

2. Improved Sample Preparation Procedures

Because we were unable to study the major region of odor interest in the standard SiO_2-10 LCC smoky-burnt fraction, several methods were sought which

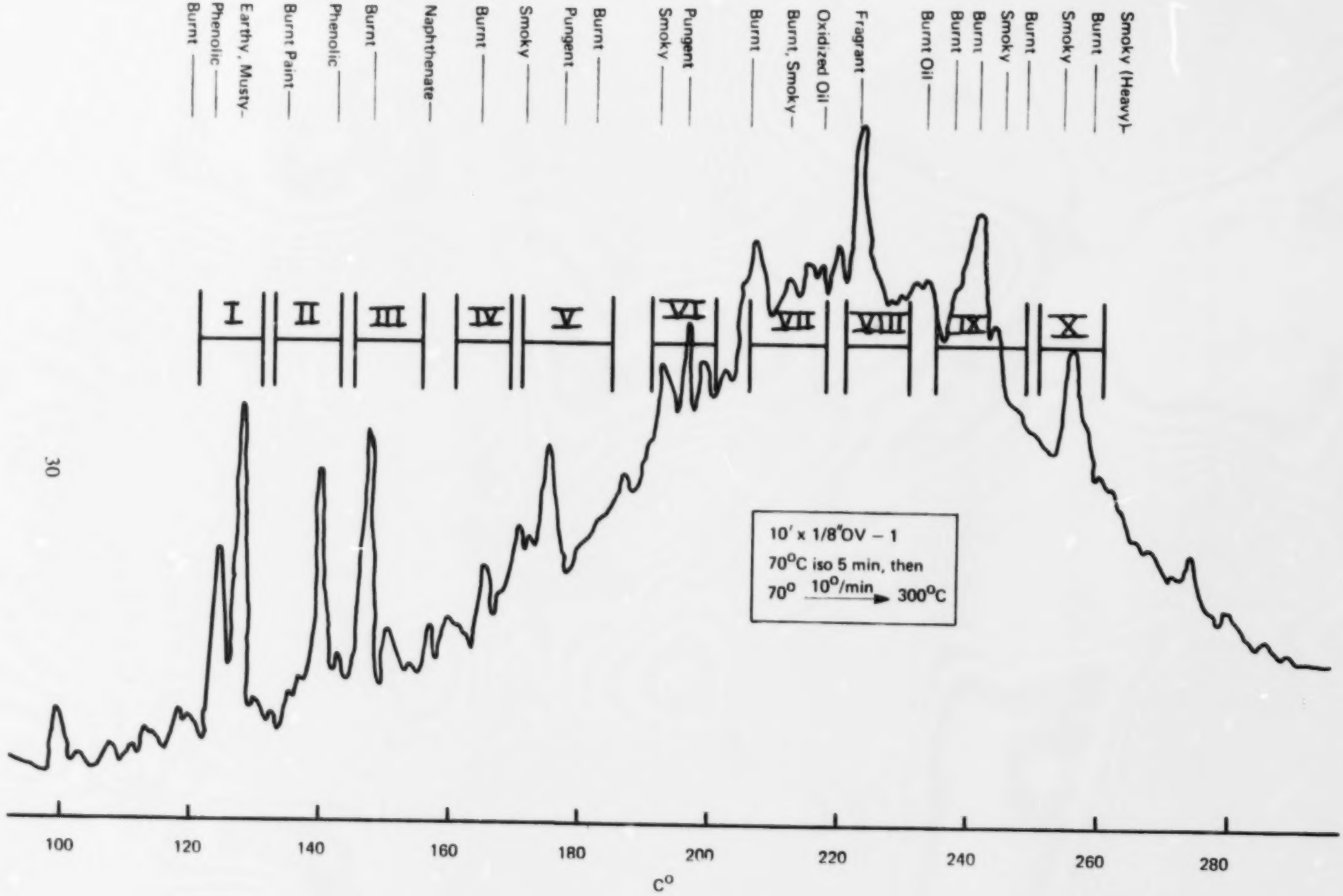

FIGURE 9 GC, ODOR PROFILE AND AREAS DESIGNATED FOR COLLECTION FROM 29A(SiO_2 - 10) ON SILICONE

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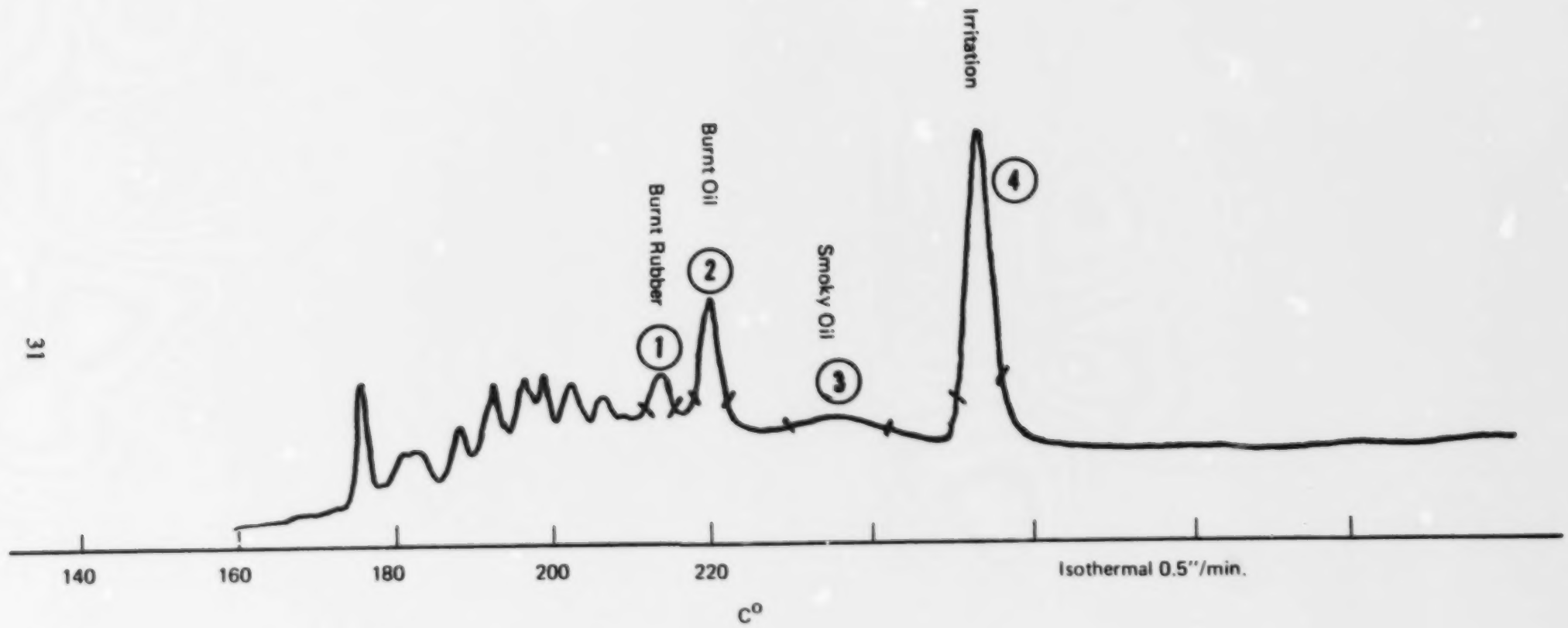


FIGURE 10 CARBOWAX CHROMATOGRAM AND ODOR PROFILE OF 29A, FRACTION I

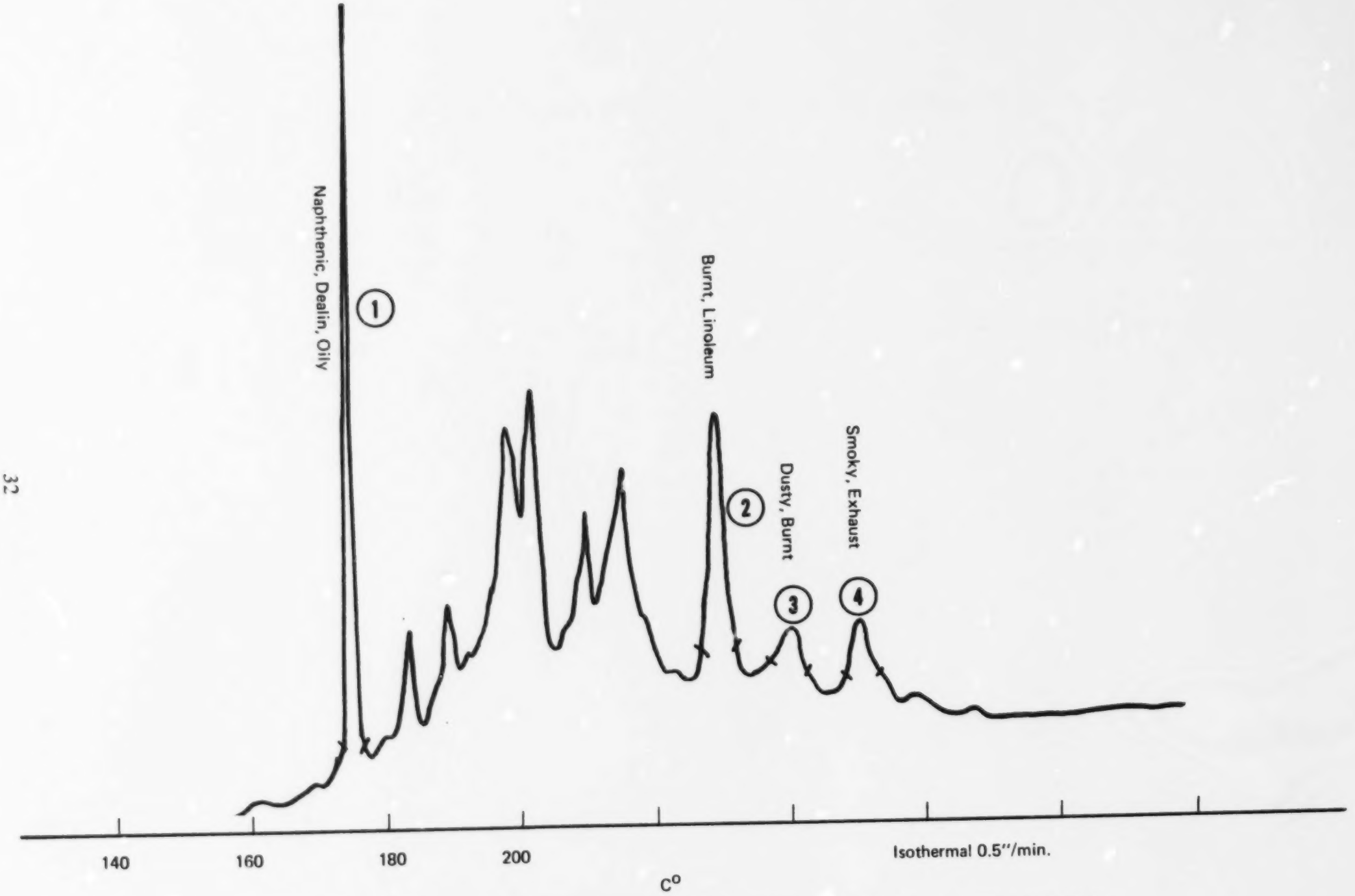


FIGURE 11 CARBOWAX CHROMATOGRAM AND ODOR PROFILE OF 29A, FRACTION II

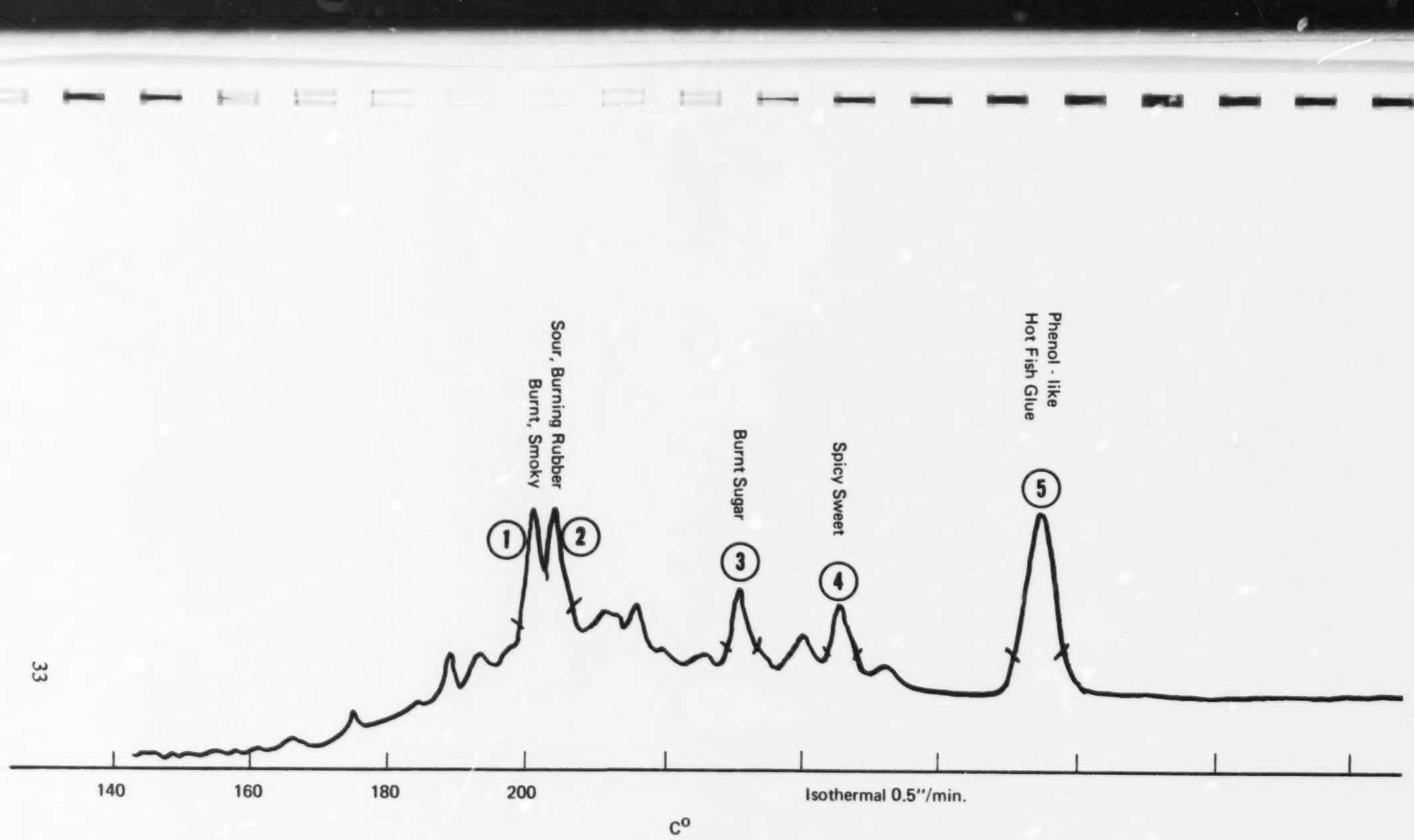


FIGURE 12 CARBOWAX CHROMATOGRAM AND ODOR PROFILE OF 29A, FRACTION III

TABLE 11

ODOR-CHEMICAL STRUCTURE DATA FOR SMOKY-BURNT SAMPLE 29A

Fraction	Peak	MW	Composition	Possible Structure	Odor
I	1	110	$C_6H_6O_2$	methyl furfural	burnt rubber
		126	$C_6H_6O_3$	methyl furoic acid	
	2	96	$C_5H_4O_2$	furfural	burnt oil
	4	94	C_6H_6O	phenol	irritation
II	1	112	C_8H_{16}	olefin	dealin, oily
	2	108	C_7H_8O	cresol	
		110	$C_6H_6O_2$	methyl furfural	burnt linoleum
		122	$C_7H_6O_2$	benzoic acid	
	3	98	$C_5H_6O_2$	furfural alcohol	dusty, burnt
	4	94	C_6H_6O	phenol	smoky
		108	C_7H_8O	cresol	
III	1	120	C_8H_8O	methyl benzaldehyde	burnt, smoky
	2	122	$C_8H_{10}O$	xylenol	sour, burnt
	3	110	$C_6H_6O_2$	methyl furfural	burnt, sugar
	5	108	C_7H_8O	cresol	irritant

would provide a more resolved odor sample which would be amenable to the two-stage GC/HRMS procedures used successfully on the oily-kerosene fraction. Some of the less successful approaches are referenced in Chapter IV. The method finally chosen is discussed here.

The principal improvements have been made by working up only the chloroform extract of the aqueous extract, by employing micro-columns, and by utilizing a more detailed gradient elution. The modified sample preparation scheme is shown schematically in Figure 13. For reporting convenience the samples prepared by this new sequence are designated by a code such as XXC-Y where XX represents the experiment number, C the chloroform extract only, and Y the fraction number from the gradient elution.

An initial trial was carried out on a small aliquot of exhaust condensate from Experiment 43. Thus, a 3000-liter chloroform aliquot (320 microliters) was dried and transferred to a 14 cm x 0.7 I.D. column packed with activated silica grade 95%. The gradient elution sequence used for the sample is given in Table 12. The major smoky-burnt odor intensities were concentrated in fractions 37 and 38. The relative mass and odor intensity observed in the initial solvent extracts for this sample were compared with those of the smoky-burnt fractions prepared as discussed here and by the standard SiO_2-10 route (Table 13). While both the pentane and chloroform extracts contain about the same amount of smoky-burnt odor, the chloroform extract contains only 3% of the mass of the total sample. In addition, the odor-to-mass ratio of fraction 38, prepared by the new LCC route, is better than that of the standard SiO_2-10 fraction. A fifteen-fold decrease in mass is obtained with only a two- to five-fold loss in odor. Thus, a net gain of about a factor of 5-10 was obtained in the odor/mass ratio. A gas chromatogram of fraction 38 on the silicone column showed a high degree of resolution with very little evidence of the "hump" which had slowed our earlier efforts.

Encouraged by this initial success, we prepared a larger sample by the new route for more complete odor and GC evaluation. The smoky-burnt odor eluted in fractions 36, 37 and 38 from the 20,000-liter sample of the chloroform extract of exhaust from Experiment 44; fractions 36 and 37 had the highest odor intensity.

The silicone gas chromatograms and odor profiles obtained for fractions 36 and 37 are shown in Figures 14 and 15. The resolution evident in these chromatograms is much better than ever previously achieved for this odor complex. The odor profiles are also quite encouraging in terms of their direct relationship to the original diesel exhaust odor. Therefore, we now believe that with this stage of resolution of the smoky-burnt odor complex, we can successfully apply the two-stage silicone-Carbowax GC/HRMS approach for the chemical identification and odor characterization of isolated single chemical species.

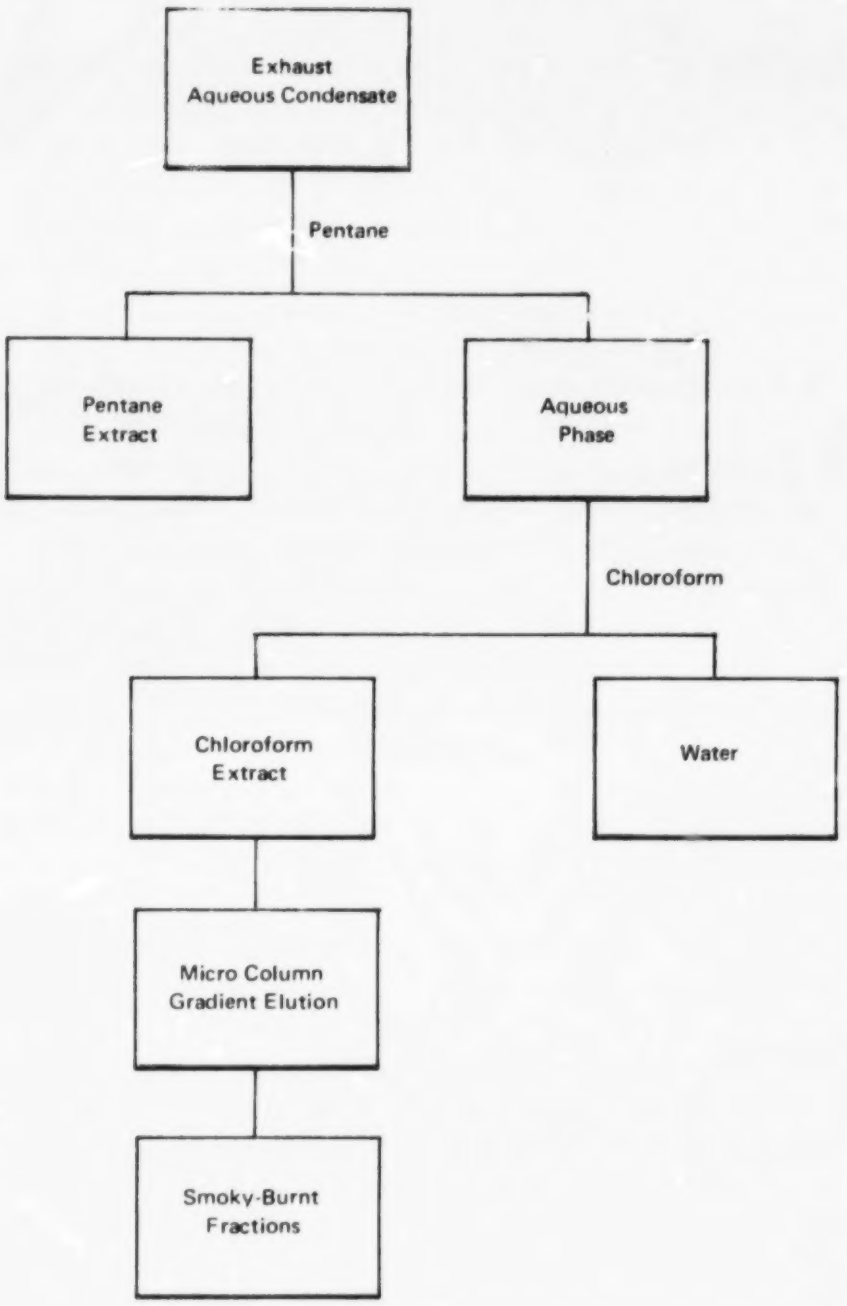


FIGURE 13 MODIFIED SMOKY-BURNT ISOLATION SEQUENCE

TABLE 12

MICRO-COLUMN FRACTIONATION OF SAMPLE 43-$CHCl_3$ EXTRACT (3,000 ℓ)

Fraction No.	Solvent	Odor Notes[3]
1 to 6	Pentane, 5 ml	
7	5% $CHCl_3$, [1], 5 ml	Kerosene
8	5% $CHCl_3$, 5 ml	
9 to 12	10% $CHCl_3$, 5 ml	
13 and 14	20% $CHCl_3$, 5 ml	
15	20% $CHCl_3$, 7 ml	
16	30% $CHCl_3$, 5 ml	
17	30% $CHCl_3$, 5 ml	
18	30% $CHCl_3$, 5 ml	
19 to 28	30% $CHCl_3$, 5 ml	
29	30% $CHCl_3$, 5 ml	
30 to 31	35% $CHCl_3$, 5 ml	
32	35% $CHCl_3$, 5 ml	
33	40% $CHCl_3$, 7 ml	Oxidized oil
34 and 35	40% $CHCl_3$, 5 ml	
36	40% $CHCl_3$, 5 ml	
37	40% $CHCl_3$, 1 ml	Smoky-Burnt
38	40% $CHCl_3$, 2.5 ml	Smoky-Burnt
39	50% $CHCl_3$, 2.0 ml	
40 to 42	50% $CHCl_3$, 5 ml	
43	50% $CHCl_3$, 5 ml	
44	50% $CHCl_3$, 5 ml	
45	75% $CHCl_3$, 5 ml	
46 to 48	75% $CHCl_3$, 5 ml	
49 and 50	$CHCl_3$, 5 ml	
51	5% MeOH[2], 5 ml	
52	5% MeOH, 5 ml	
53	10% MeOH, 5 ml	Sour

1. % $CHCl_3$ in pentane
2. % MeOH in $CHCl_3$
3. Blotter Strip

TABLE 13

MASS ODOR COMPARISONS OF SMOKY-BURNT FRACTIONS[a]

Sample	Mass		Odor[d]	
	FOE/1000 ℓ (mg)[e]	Percent	TIA	SB
Pentane Extract	66	97	1½	1½
Chloroform Extract	2	3	1-2	1½
43-SiO_2 10[b]	0.6	1	1½	1½
43C-38[c]	0.04	0.06	1	1

a. Experiment 43

b. "Standard" SiO_2-10 Fraction

c. Fraction 38 as shown in Table 12

d. Test Room Evaluation – 200

e. FOE/1000 ℓ = Fuel oil equivalent per 1000 ℓ of exhaust

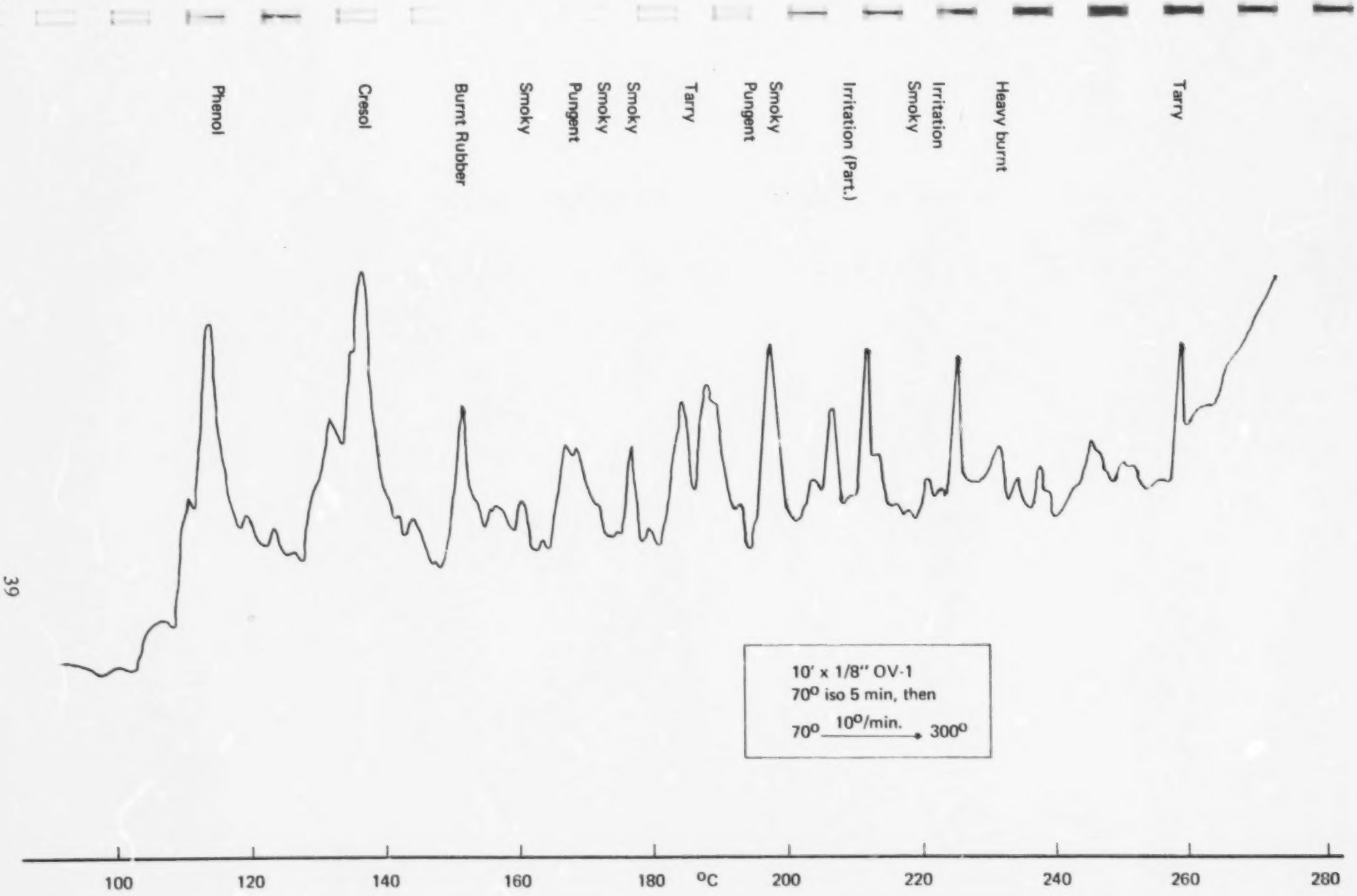


FIGURE 14 SILICONE GAS CHROMATOGRAM OF SMOKY-BURNT FRACTION 44C-36

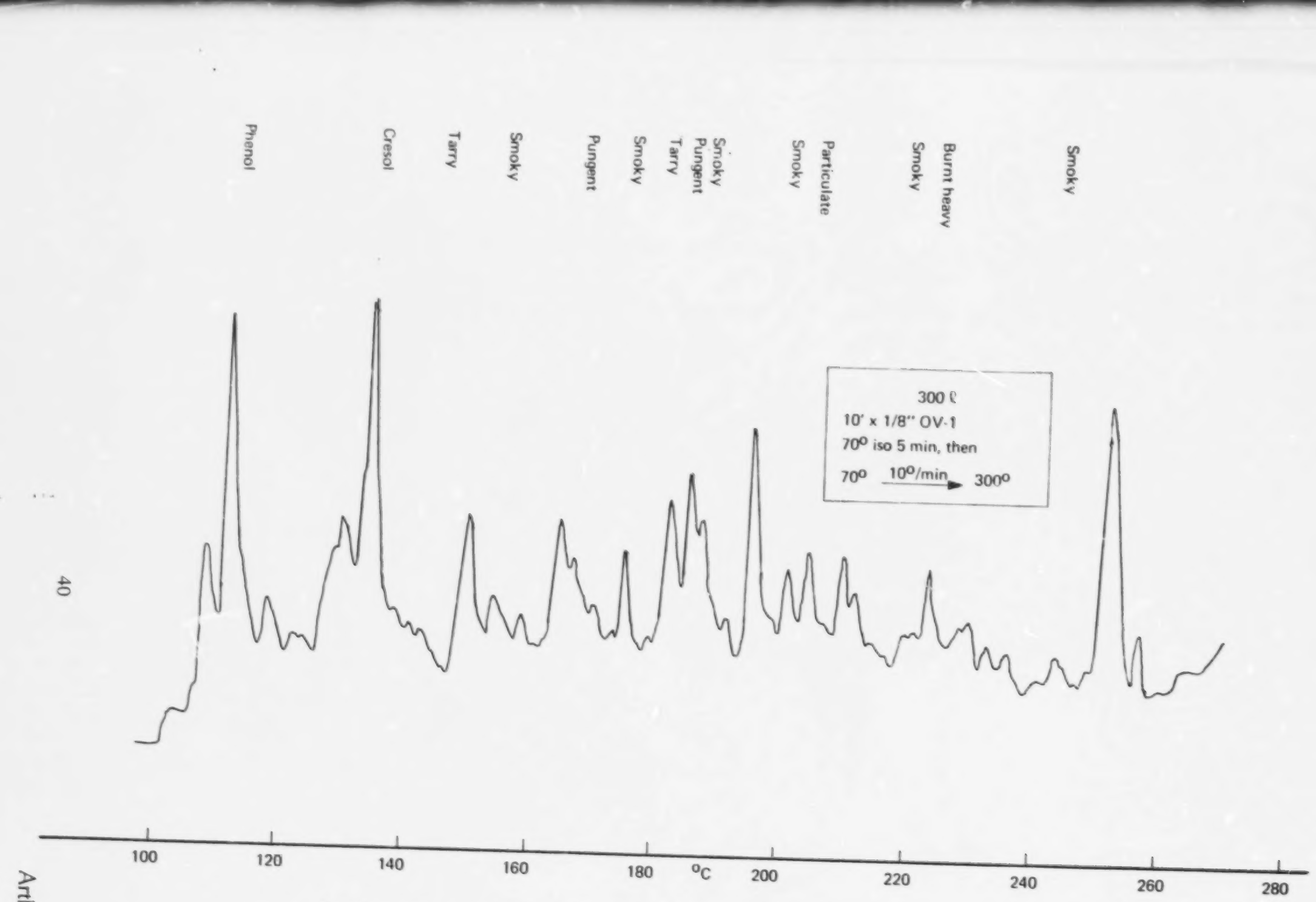


FIGURE 15 SILICONE GAS CHROMATOGRAM OF SMOKY-BURNT FRACTION 44C-37

3. Preliminary Chemical Identification Studies

Because of operational difficulties at the end of the current year's program we were unable to combine the clean-up scheme discussed above and our two-stage GC-MS identification procedure. However, in order to gain some preliminary insights into the types of chemical classes involved throughout the smoky-burnt odor complex, we did carry out a few high-resolution mass spectrometry studies on the compounds eluting from just the first-stage silicone gas chromatogram. For comparison purposes a sample was prepared by the new chloroform method (45C-23) as well as a sample by the standard SiO_2-10 route (45-10). The exhaust for both samples was obtained from Experiment 45, 10,000 liters being submitted to the standard first-stage chromatograph, and the chloroform extract from the remaining 50,000 liters was fractionated by the new method. In this elution, the smoky-burnt odor came out earlier than in Experiment 43 or 44 and fraction 23 (coded 45C-23) contained the most intense smoky-burnt odor character. The silicone GC and odor profiles obtained for 45-10 and 45C-23 are shown in Figures 16 and 17, respectively.

Sample 45C-23 shows the excellent resolution anticipated from our preliminary studies. Surprisingly, 45-10 also shows better resolution than we have usually obtained from the standard LCC procedures in the past. However, the 45-10 sample still contains more of a "hump" than we could hope to resolve by the two-stage GC method.

Several regions were selected in each chromatogram on the basis of odor importance, and high-resolution mass spectra were obtained on these regions. The regions studied are indicated by peak numbers on each trace. Some of the HRMS chemical data obtained for the samples are given in Tables 14 and 15 for 45C-23 and 45-10, respectively. It is important to remember that each of these GC peaks still represents many compounds because only one GC separation step was used.

In the tables, we have indicated the odor associated with particular peaks and the major mass species observed by HRMS in the same region. In some cases tentative chemical classes have been assigned. The purpose of this work was to expand our knowledge of the chemical types present in order to aid the future, more refined, identification efforts. While particular species are observed in regions of odor interest, we are not at all certain that the odor itself is indeed associated with any of the major species. Recalling the oily-kerosene studies, it was not unusual to find the odor in a silicone GC profile to be associated with a minor component of the peak.

We have not yet had the opportunity to fully evaluate these data, but certainly there is a tremendous diversity of chemical species in these samples. The identifications will resolve more clearly when we use the two-stage GC approach. The possible structure choices indicated in the tables are in many cases not unique

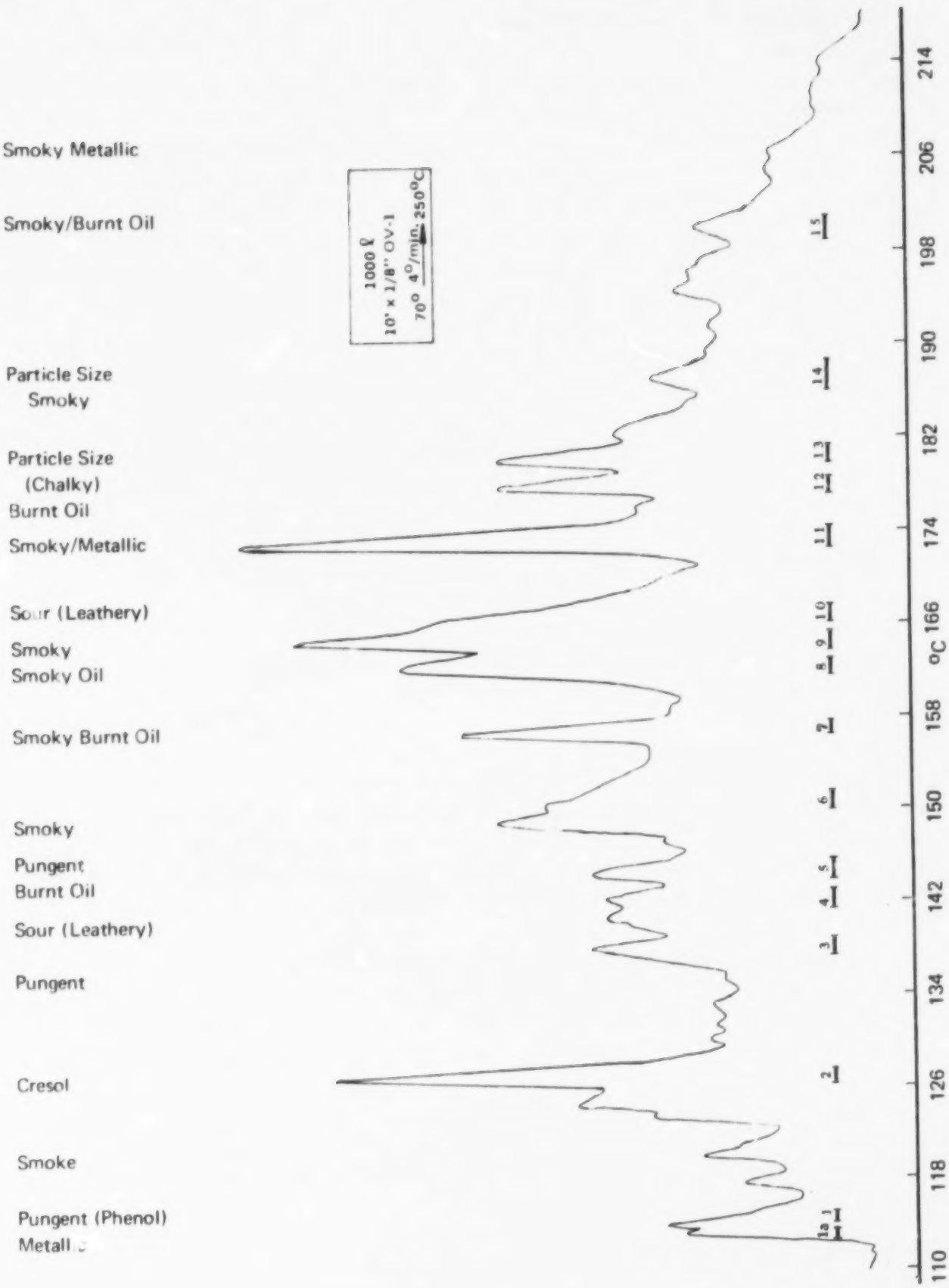


FIGURE 16 SILICONE GAS CHROMATOGRAM AND ODOR PROFILE OF SMOKY-BURNT 45C-23

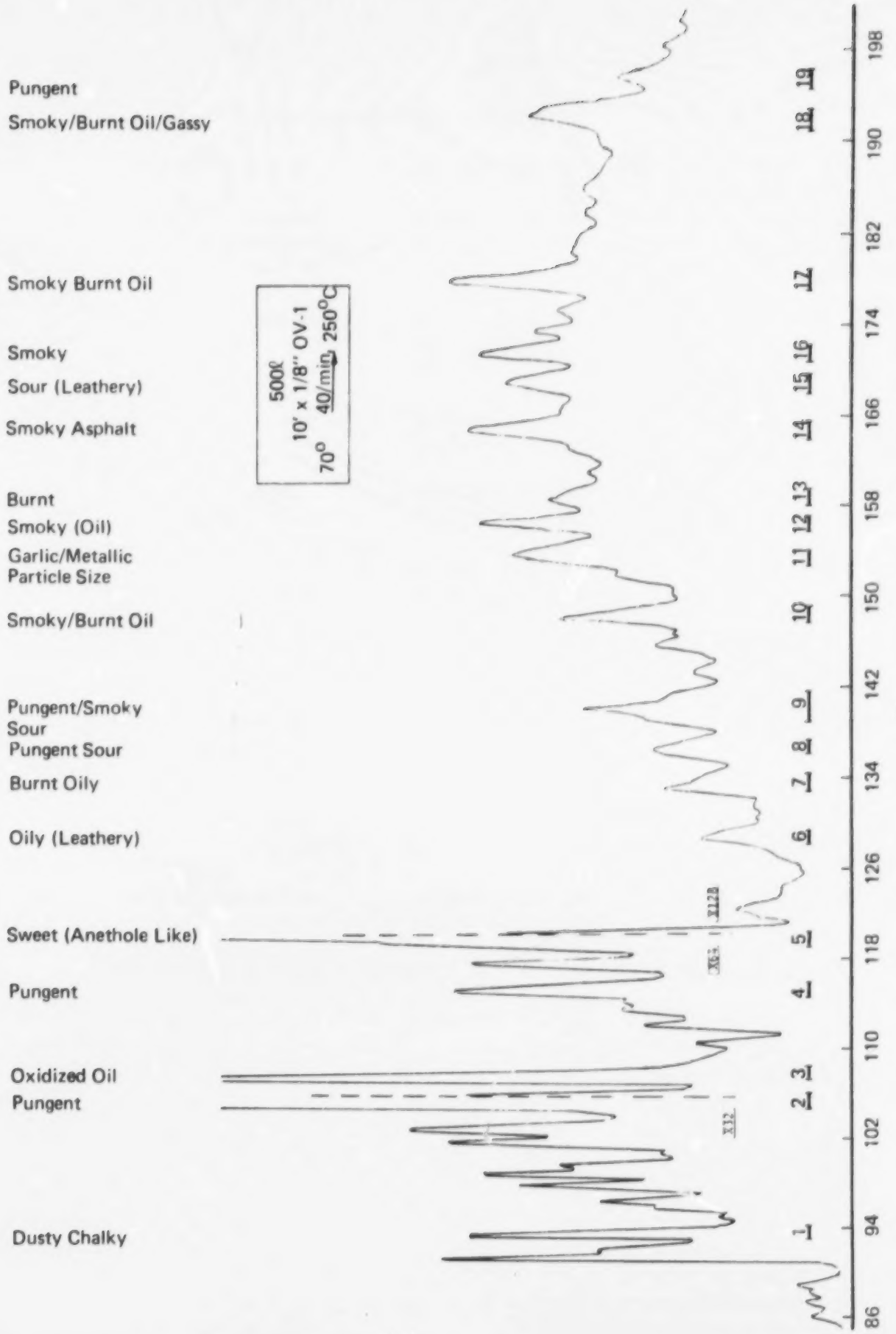


FIGURE 17 SILICONE GAS CHROMATOGRAM AND ODOR PROFILE OF SMOKY-BURNT 45 - 10

TABLE 14

45C-23 SMOKY BURNT PRELIMINARY HRMS RESULTS

Peak	Odor	MW[a]	Composition	Possible Chemical Class[b]
1a	metallic	96	C_6H_8O	dienone
		106	C_7H_6O	benzaldehyde[c]
		110	$C_6H_6O_2$	furfural
1	pungent (phenol)	94	C_6H_6O	phenol[c]
2	cresol	108	C_7H_8O	cresol[c]
4	sour (leathery)	122	$C_8H_{10}O$	xylenol[c]
		124	$C_7H_8O_2$	furfural
5	burnt oil	130	C_9H_6O	indenone
		136	$C_8H_8O_2$	phenyl carboxylic
6	smoky	134	$C_8H_6O_2$	--
		136	$C_9H_{12}O$	phenol
7	smoky/burnt oil	132	C_9H_8O	indanone
		134	$C_9H_{10}O$	phenyl carbonyl
8	smoky oil	146	$C_9H_6O_2$	benzofurfural
		148	$C_{10}H_{12}O$	phenyl carbonyl
		150	$C_8H_6O_3$	--
9	smoky	148	$C_9H_8O_2$	phenyl propenoic acid
		150	$C_{10}H_{14}O$	phenol
10	sour (leather)	148	$C_9H_8O_2$	phenyl propenoic acid
		162	$C_9H_6O_3$	--
11	smoky (metallic)	146	$C_9H_6O_2$	benzofurfural
		148	$C_9H_8O_2$	phenyl propenoic acid
		158	$C_{10}H_6O_2$	naphthoquinone[c]
13	particle size (chalky)	162	$C_{10}H_{10}O_2$	phenyl propenoic acid
		164	$C_9H_8O_3$	--
14	particle size/smoke	156	$C_{11}H_8O_2$	naphthaldehyde
		160	$C_{10}H_8O_2$	benzofurfural
		172	$C_{11}H_8O_2$	naphthoic acid
		176	$C_{11}H_{12}O_2$	phenyl propenoic acid

a. Major species present in peak
b. Chemical class -- alkyl groups not indicated
c. Probably correct structure assignment

TABLE 15

45-10 SMOKY-BURNT PRELIMINARY HRMS RESULTS

Peak	Odor	MW[a]	Composition	Possible Chemical Class[b]
1	dusty/chalky	96	$C_5H_4O_2$	furfural
2	pungent	106	C_7H_6O	benzaldehyde[c]
		110	$C_6H_6O_2$	furfural
3	oxidized oil	94	C_6H_6O	phenol[c]
		96	C_6H_8O	dienone
4	pungent	108	C_7H_8O	cresol
		122	$C_7H_6O_2$	benzoic acid
5	sweet	120	C_8H_8O	phenyl carbonyl
		124	$C_7H_8O_2$	furfural
6	oily (leathery)	122	$C_8H_{10}O$	xylenol[c]
		134	$C_9H_{10}O$	phenyl carbonyl
		138	$C_8H_{10}O_2$	furfural
7	burnt oily	122	$C_8H_{10}O$	phenol
		134	$C_9H_{10}O$	phenyl carbonyl
8	pungent sour	122	$C_7H_6O_2$	phenyl carboxylic
		130	C_9H_6O	indenone
		138	$C_9H_{14}O$	dienone
9	pungent/smoky	134	$C_8H_6O_2$	---
		138	$C_8H_{10}O_2$	furfural
		148	$C_{10}H_{12}O$	phenyl carbonyl
10	smoky/burnt oil	146	$C_{10}H_{10}O$	indenone
		150	$C_9H_{10}O_2$	phenyl carboxylic
		152	$C_8H_8O_3$	---
11	metallic/particle size	164	$C_{10}H_{12}O_2$	phenyl carboxylic
		168	$C_{10}H_{16}O_2$	---
12	smoky	148	$C_9H_8O_2$	---
		162	$C_{11}H_{14}O$	phenyl carbonyl
		180	$C_{12}H_{20}O$	dienone
13	burnt	168	$C_{10}H_{16}O_2$	---
		194	$C_{13}H_{22}O$	dienone
14	smoky/burnt	146	C_9H_6O	benzofurfural
		180	$C_{11}H_{16}O$	furfural

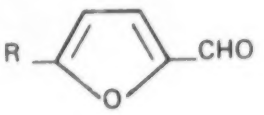
TABLE 15 (Continued)

Peak	Odor	MW[a]	Composition	Possible Chemical Class[b]
15	sour (leathery)	176	$C_{12}H_{16}O$	phenyl carbonyl
16	smoky	148	$C_9H_8O_2$	phenyl propenoic acid
		194	$C_{12}H_{18}O_2$	furfural
		208	$C_{14}H_{24}O$	dienone
17	smoky/burnt oil	156	$C_{11}H_8O$	naphthyl carbonyl
18	smoky/gassy	170	$C_{12}H_{10}O$	naphthyl carbonyl
		188	$C_{13}H_{16}O$	indanone
		222	$C_{15}H_{26}O$	dienone
19	pungent	176	$C_{11}H_{12}O_2$	phenyl propenoic acid
		186	$C_{12}H_{10}O_2$	naphthoic acid

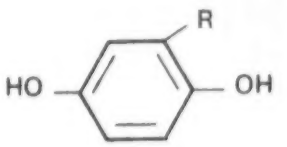
a. Major species present in peak
b. Chemical class – alkyl groups not indicated
c. Probably correct structure assignment

and several other isomeric choices are possible. The assignments for phenol, cresol, benzaldehyde, etc. (i.e., the simpler species) are most likely correct. At this time, however, it is not possible to distinguish, for instance, between furfurals and hydroquinones. Several isomeric groups of structures which are possible in these samples are indicated below:

Composition $C_6H_6O_2$ + R

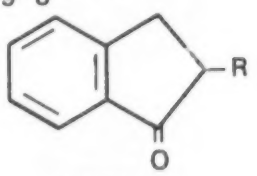


furfurals

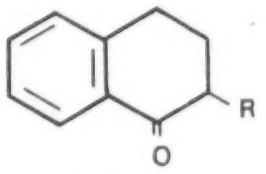


hydroquinones

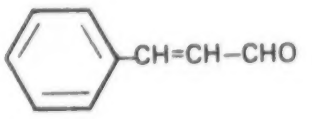
Composition C_9H_8O + R



indanones

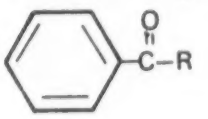


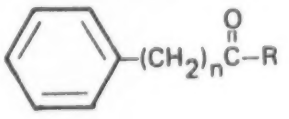
tetralones

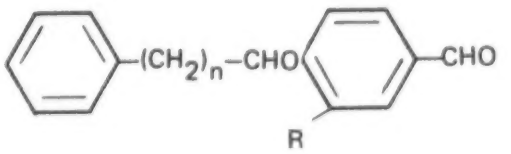


cinnamaldehyde

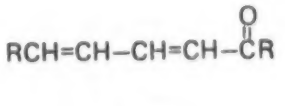
Composition C_8H_8O + R, phenyl carbonyls



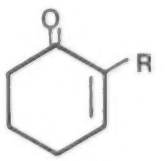




Composition C_6H_8O + R

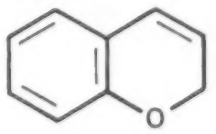


dienones

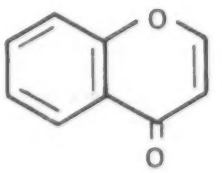


cyclohexenones

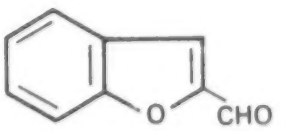
Composition $C_9H_6O_2$ + R



isocoumarin

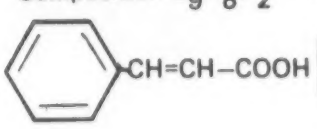


coumarin

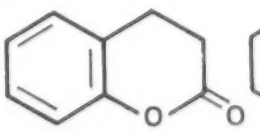


benzofurfural

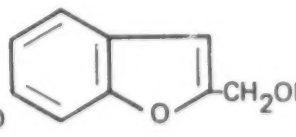
Composition $C_9H_8O_2$ + R



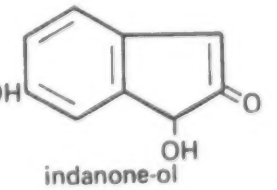
phenyl propenoic acid



dihydro isocoumarin



benzofurfural



indanone-ol

These examples are meant only to illustrate the type of isomerism possible and not to include all of the other possible choices. Since the spectral data on these samples are still quite complicated (too many unresolved compounds), it would be premature to try and attach too much significance to the data. We have not made any effort to represent the large degree of overlap which actually occurs between these samples. The compounds listed were observed, but others not listed were also present, and it is difficult to know at this time whether the compositions we have chosen to present here represent the odors of interest.

IV. SUPPORTING STUDIES

Several studies which supported our research on the chemical structure identification of odorous diesel exhaust compounds are reported in a series of Appendices.

In the period between Experiments 42 and 43 (November 1969) a new supply of diesel fuel was obtained. A comparison of the old (year 1) and new (year 2) fuels is given in Appendix F.

The efforts of chemical treatment on the odor behavior of exhaust and fuel samples described in Appendix G have helped in our understanding of the relationship between chemical structure/reactivity and odor.

The condensate from the heptane fueled engine at General Motors was briefly examined for comparison of the nature of exhaust products relative to that obtained with normal diesel fuel. The details are given in Appendix H.

In addition to several studies exploring new adsorption and partition LCC approaches for the separation of the smoky-burnt odor complex, we conducted a preliminary evaluation of the potential of gel permeation chromatography (GPC) to achieve the resolution desired through a basically different approach. The GPC work is reported in Appendix I.

APPENDIX A

ODOR PROFILE TECHNIQUE

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APPENDIX A

ODOR PROFILE TECHNIQUE*

1. SUMMARY

The standard diesel exhaust sample has been defined as a 2½-min. post-muffler exhaust aliquot of 21ℓ taken during normal engine operation and a 25 kw (30%) load after warm-up. The profile analysis of the standard sample diesel exhaust was consistent from day to day, but the odor of diesel exhaust did show some differences with variations in engine operation. Preliminary studies indicate that within the normal procedural time interval between sampling and examination, there are no detectable losses. Indeed, the odor appears to persist with only slight change for over one hour. Total profile characterization is consistent with the odor observed when traveling behind a bus, which confirms our belief that the mode of engine operation provided a representative sample for analytical studies.

The description of the diesel exhaust odor in the test room with a dilution ratio of 600:1 can be described by three character notes: *oily*, represented by technical grade hexadecane among other standards; *burnt*, which, although similar to a low dilution of propionaldehyde, phenol, and cresol, is produced in fuels with partial oxidation at elevated temperatures, and *kerosene*, which is the top odorous component of the fuel and may be described as having sweet, sharp, sour, tarry, and solvent components. In addition to these odor characteristics which appeared in the slight-to-moderate intensity range at this dilution, two feeling sensations – nose irritation and eye irritation – were apparent.

As implied by the descriptive terminology used, some of the odor characteristics are present in the fuel itself. The odor characterization of a 150μℓ aliquot of fuel, which (by computation) is equivalent to the amount of fuel burnt to produce the 21-ℓ sample of exhaust, produces an odor in the test room at least as strong as the exhaust odor. The dominant odor characteristic is kerosene, with the oily note being less intense and the burnt aroma barely detectable. With the diesel exhaust, the oily and burnt aromas are the primary character notes and kerosene a supplementary factor.

2. ODOR PROFILE METHODOLOGY

The Odor Profile Method of analysis has proven useful in flavor and odor studies in a wide range of food and nonfood products. The Profile Method, which originated at Arthur D. Little, Inc., 25 years ago, is a semiquantitative and

* Taken from Final report of first year's work, July 1969, "Chemical Identification of the Odor Components in Diesel Engine Exhaust."

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qualitative description of the odor sensation. The total odor sensation can be described by six character notes. The method is qualitative in that there is verbal description as to the odor quality(s) perceived. The order of appearance of odor character notes indicates the other odor qualities present as a function of time on a microsecond basis.

The intensity of each character note (as well as the Total Intensity of Aroma, TIA) is rated on a four-point scale ranging from threhold-) (, slight 1, moderate- 2, to strong- 3 intensities. It has been our experience that for the odor intensity to increase by one unit (i.e., from slight to moderate), a ten-fold increase in concentration is required. The threshold intensity indicates that the character note detected is just recognizable. The basic four point scale of threshold-)(– to strong- 3 – intensity can be expanded into a seven point scale with experienced panelists by the use of one-half ratings. Thus, the full scale of intensity rating of the odor strength is summarized below.

Numerical Rating	Intensity
)(	Threshold (recognition)
1/2	Very Slight
1	Slight
1½	Slight to Moderate
2	Moderate
2½	Moderate to Strong
3	Strong

The presence of feeling sensations is indicated by a check mark(√) without any effort to describe their intensity. Four trained analysts form the odor profile panel. The sample to be analyzed is presented to the panelists in a standard manner. In this study, each of the four panelists entered the odorized test chamber independently of one another and sniffed the air three times. Each then recorded his observations on the odor character notes perceived, their order of appearance, and their intensity. After the observations in the test room, the panelists gathered to discuss their results. Reference was made to odor standards to relate the various verbal descriptions used and to develop a common language in describing the odor quality. Reference odor standards may be single chemical species or may refer to a mixture of chemicals.

The panel's results were then composited into an odor profile that summarized the odor observations of the four panelists and indicated the odor quality, the order of appearance of the characteristic notes and their intensities.

3. ODOR TEST ROOM

The Odor Test Room consisted of an antechamber, an odor chamber, and supporting equipment such as fans, ducts, activated carbon, air intake, and air exhaust motors. The air is treated with activated carbon (C-42 cannister from Dorex) and provided a low-odor background diluting medium and was also used to flush odorized air from the chamber and acclimate the four panel members to a low odor background. The odor chamber where the odor studies were carried out was an aluminum-clad room with a volume of 12,600ℓ . Previous studies have shown polished aluminum to be satisfactory for odor studies because it has a low odor background. Fans in both the odor chamber and antechamber ensured adequate mixing and assisted in flushing the test room with odor-free air.

The sequence of events occurring prior to an odor observation by the panel in the test room is listed below.

a. Odor-free air is used to flush out the antechamber and odor chamber.

b. The door connecting the odor chamber and antechamber is closed thus sealing the odor chamber.

c. Diesel exhaust is injected into the odor chamber through a sampling line by means of a swivel-jointed sampling system. Three fans located in the odor chamber circulate the diesel exhaust with the diluting air to ensure proper mixing. Five minutes after injection the fans are shut down, and the odorized air in the odor chamber is allowed to come to rest.

d. The four panel members then enter the antechamber where they become acclimated to the low odor background air.

e. The panel then enters the odor chamber, one at a time, to make observations.

f. The cycle is then repeated to prepare the odor test room for the next observation. A 20-minute flushing period has been found to be adequate for removing odor from the test room.

4. ODOR ANALYSIS – DIESEL TEST SAMPLES

Reference odor profiles on diesel exhaust itself have been developed using a 21-ℓ injection of exhaust into the odor test room (600/1 dilution). Because the condensation sample collection procedure collects only about 10% of the odor in the condensate, it is necessary to inject 210-ℓ aliquots of the extracted fractions into the test room for their odor evaluation.

APPENDIX B

STANDARD LIQUID COLUMN CHROMATOGRAPHIC SEPARATION PROCEDURE

APPENDIX B

STANDARD LIQUID COLUMN CHROMATOGRAPHIC SEPARATION PROCEDURE*

In the standard first-stage separation technique, the sample is subjected to silica liquid-column chromatography. The detailed experimental conditions are as follows using the 76,500 liters of exhaust collected in Experiment 25 as an example:

Column Conditions. 1.8 cm ID packed for a length of 20 cm with silica, Grade 950 (Fisher Scientific, 60 to 200 mesh) activated at 110°C for two hours.

Sample Preparation. A small volume (15 ml) of organic condensate extract was mixed with 15 ml silica and transferred to the top of the column.

Elution Scheme. Refer to Table B-1.

Handling of Various Fractions. All fractions were allowed to evaporate overnight at room temperature and the final volume was adjusted to 7.65 ml in each case. Thus, for these examples representative of 76,500ℓ of exhaust, a 2.1μℓ aliquot represented a standard injection of 21ℓ of exhaust.

The fractionation of the sample, along with the elution scheme and qualitative odor is given in Table B-1. Oily kerosene comes out in fractions 4 or 5 and the smoky-burnt odor character comes out in fraction 10. Since the total Sample 25 had a fuel oil equivalent (FOE) of about 5,000 mg,**about 70% of the mass was in fraction 1, 14% in fraction 5, and only 3% in fraction 10.

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*Taken from Final report of first year's study, July 1969, "Chemical Identification of the Odor Components in Diesel Engine Exhaust."

**Mass determined by a gas chromatograph flame ionization detector (GC FID) response relative to fuel oil calibration.

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TABLE B-1

SILICA LCC ELUTION SCHEME AND ODOR OBSERVATIONS FOR SAMPLE 25

Fraction	Solvent	Comment	FOE (mg) [a]	Odor [b]
1	Pentane, 150 ml [c]	Colorless effluent	3,500	Odorless
2	Pentane, 100 ml	Colorless effluent		
3	Pentane, 100 ml	Colorless effluent		
4	Benzene, 100 ml	The yellow component starts moving down upon addition of benzene; collected effluent was still colorless		
5	Benzene, 100 ml	Greenish yellow effluent	700	Oily, kerosene
6	Benzene, 100 ml	Greenish yellow		
7	$CHCl_3$, 150 ml	Light greenish yellow		
8	5%MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
9	10% MeOH/$CHCl_3$, 100 ml	Very light greenish yellow		
10	25% MeOH/$CHCl_3$, 100 ml	Brown	150	Smoky-burnt, oily
11	50% MeOH/$CHCl_3$, 100 ml	Brownish yellow		
12	MeOH, 125 ml	Yellow		

a – Fuel oil equivalent; weight of sample based on GC response compared to fuel oil calibration using the FID response from silicone column. Total FOE for Sample 25 =5000 mg.

b – Qualitative odor screening observation.

c – The eluted fractions were concentrated to 7.65 ml.

APPENDIX C

IMPROVED GAS CHROMATOGRAPHIC TRAPPING TECHNIQUES

APPENDIX C

IMPROVED GAS CHROMATOGRAPHIC TRAPPING TECHNIQUES

Our prior approach to trapping gas chromatographic fractions for further resolution on a second GC column and for GC-MS had led to some difficulties. The basic problem was that the method of trapping on cold glass beads resulted in a diluted sample because the sample had to be removed with solvent. The complications which arose were that further examination of the solution by GC required ten times more sample than was needed for the analysis itself. This in turn usually necessitated the collection and recombination of many trapped fractions, which led to a loss of some of the original GC resolution. The large amounts of solvent used in the GC-MS studies also caused pressure problems in the source of the mass spectrometer.

We have now developed a technique based on the approach published by Bierl *et al.*,[1] whereby fractions eluting from the GC at any elevated temperature and over variable time spans may be trapped with at least 90% efficiency for rechromatography on a second column.

The traps are 5½-inch x 1/8-inch lengths of stainless steel tubing packed with silicone GC column packing (10% OV-1 on 100/120 mesh Gas Chrom Q). Fractions are trapped by placing the traps at the exit of the GC column effluent splitter on the PE 900 used for odor profile studies. The traps are designed to slide directly into the injector of the Varian 1200 by removing the septum and nut, inserting the trap, and replacing the septum nut. The entire injection sequence can be completed in 10 seconds. The GC column is maintained at room temperature during the injection so that any premature sample bleed will be caught at the front end of the column. The geometry of the trap and injector port is such that the ends of the trap are pressed tight between the septum and the front of the column. Carrier gas flow through the trap (rather than leakage around it) is then assured by having two 1/16-inch diameter holes drilled ½-inch from the front (septum end) of the trap.

Using this approach, we have repetitively and now routinely trapped a number of fractions from both silicone and Carbowax columns. Prior trapping efforts from Carbowax using the glass beads were always unsuccessful. Fractions are trapped with about 90% efficiency, and the trapped fractions retain their original resolution when reexamined under the original trapping conditions.

In addition to the retention of resolution, the real value of this approach is that, from a single sample injection, we can trap fractions and rechromatograph the entire fraction for MS or odor studies.

1. B.A. Bierl, M.Beroza, and J.M. Ruth, *Anal. Chem., 40,* 286 (1968).

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APPENDIX D

CARBOWAX GAS CHROMATOGRAMS OF SILICONE PEAKS THAT CONTAIN ODORS RELATED TO THE OILY KEROSENE ODOR COMPLEX

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APPENDIX D

CARBOWAX GAS CHROMATOGRAMS OF SILICONE PEAKS THAT CONTAIN ODORS RELATED TO THE OILY KEROSENE ODOR COMPLEX

As discussed in Section IIIA, fraction 38-4 from an LCC separation experiment was subjected to two-stage gas chromatography for further purification of the odor containing compounds. Selected peak areas from a silicone column were trapped and rechromatographed on a carbowax column. The following figures represent the gas chromatographic, mass spectrometric, and odor data for these silicone peaks.

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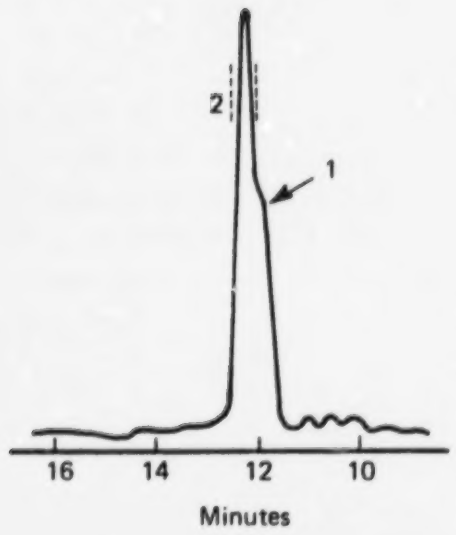
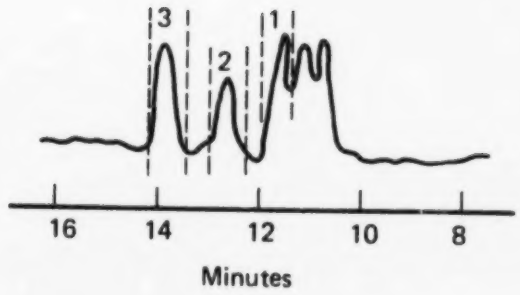


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
2	2	134	$C_{10}H_{14}$ alkyl benzene	musty oily

a. Approximate percentage of total 38-4 fraction.

FIGURE D-1 SILICONE PEAK 4 ON CARBOWAX

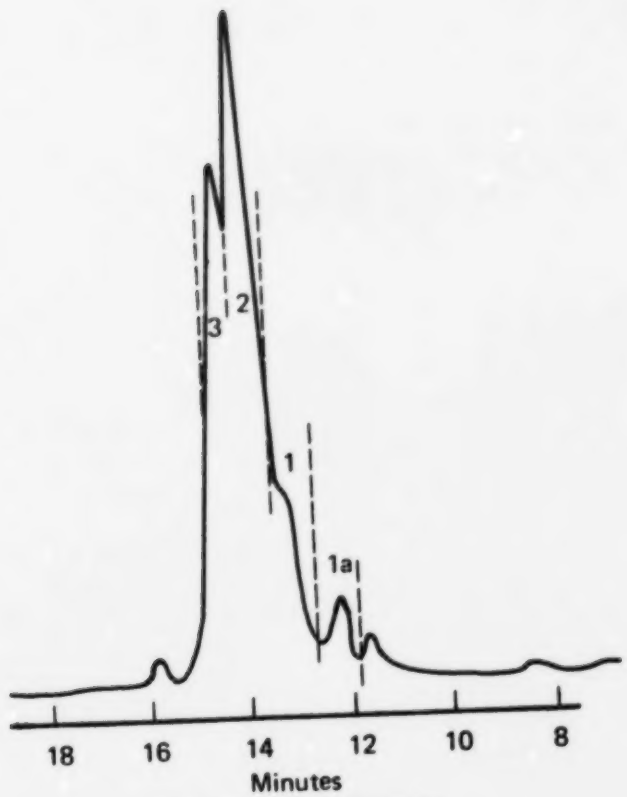


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.2	148	$C_{11}H_{16}$ alkyl benzene	strong-uncharacterized
2	0.2	134	$C_{10}H_{14}$ alkyl benzene	tarry
3	0.2	132	$C_{10}H_{12}$ tetralin	rubbery sulfide

a. Approximate percentage of total 38-4 fraction.

FIGURE D-2 SILICONE PEAK 5/6 ON CARBOWAX

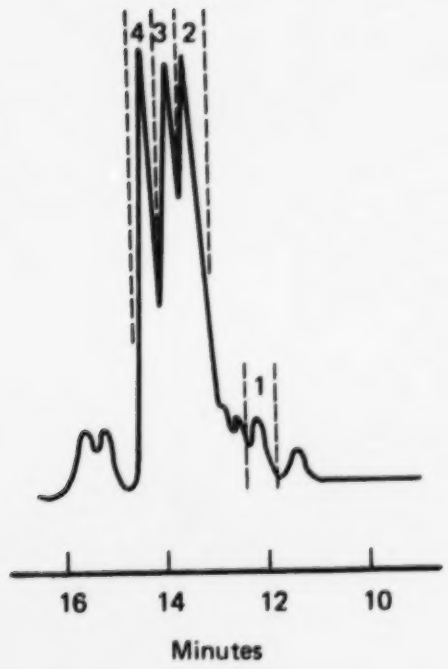


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1a	0.05	162	$C_{12}H_{18}$ alkyl benzene	wax
1	0.05	160	$C_{12}H_{16}$ dimethyltetralin	kerosene
2	1	148	$C_{11}H_{16}$ alkyl benzene	kerosene
3	0.1	146	$C_{11}H_{14}$ dimethylindan	kerosene

a. Approximate percentage of total 38-4 fraction.

FIGURE D-3 SILICONE PEAK 7 ON CARBOWAX

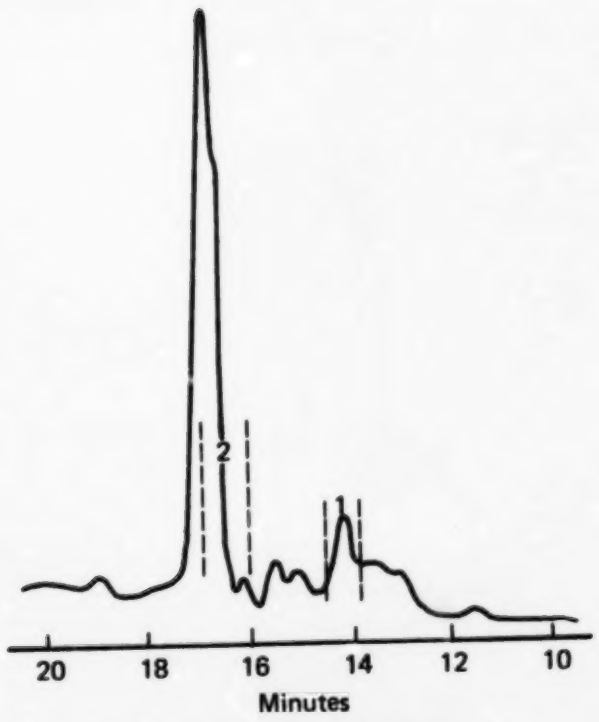


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.1	162	$C_{12}H_{18}$ alkyl benzene	irritation
2	0.3	160	$C_{12}H_{16}$ alkyl indan or tetralin	indole like
3	0.3	148	$C_{11}H_{16}$ alkyl benzene	oily metallic
4	0.3	148	$C_{11}H_{16}$ alkyl benzene (isomer)	oily

a. Approximate percentage of total 38-4 fraction.

FIGURE D-4 SILICONE PEAK 8 ON CARBOWAX

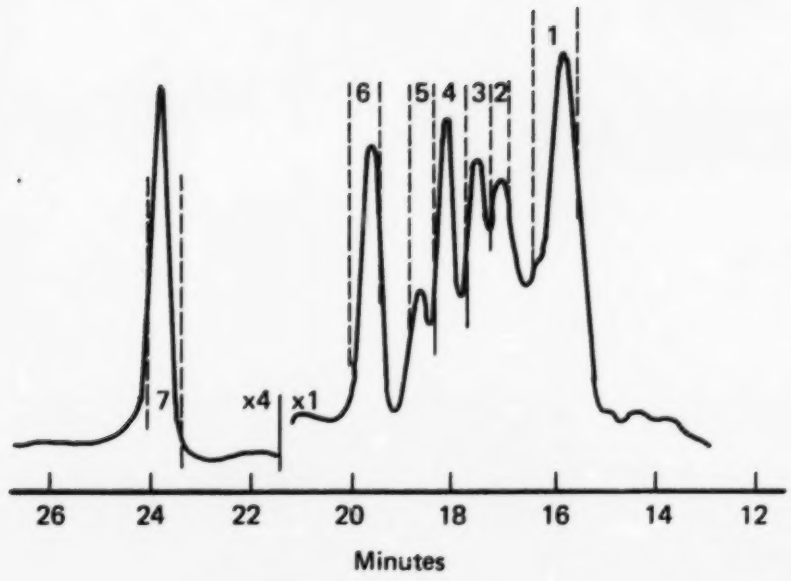


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.2	162	$C_{12}H_{18}$ alkyl benzene	rubbery (but not sulfur)
2	2	146	$C_{11}H_{14}$ methyltetralin	naphthenate

a. Approximate percentage of total 38-4 fraction.

FIGURE D-5 SILICONE PEAK 10 ON CARBOWAX

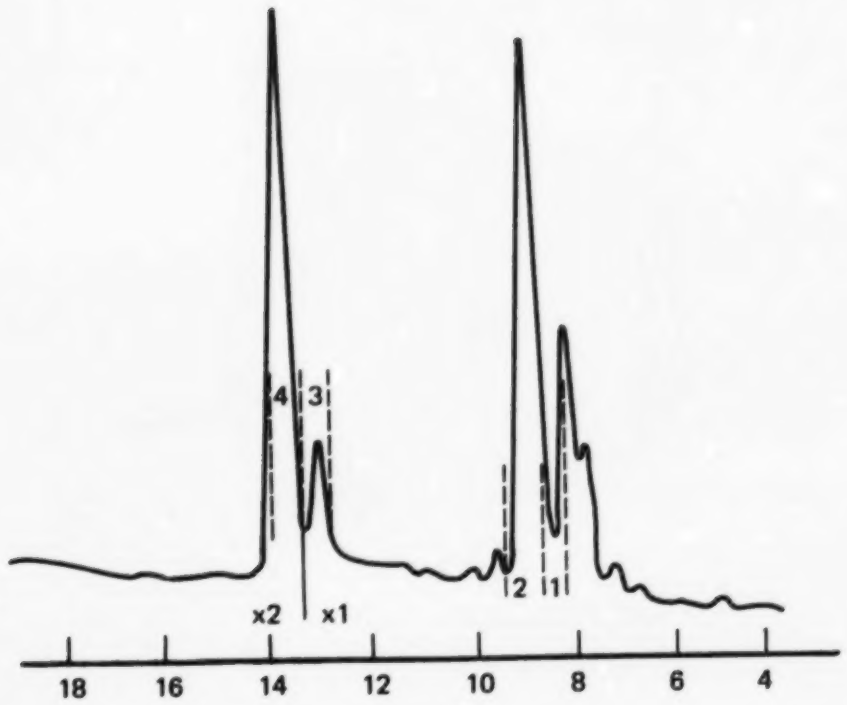


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	1	162	$C_{12}H_{18}$ (alkyl benzene)	napthenate
	0.1	174	$C_{12}H_{18}$ (trimethyltetralin)	
2	0.5	160	$C_{12}H_{16}$ dimethyl tetralin	–
3	0.5	160	$C_{12}H_{16}$ trimethylindan	kerosene
4	1	148	$C_{11}H_{15}$ alkyl benzene	–
5	0.5	146	$C_{11}H_{14}$ dimethylindan	light kerosene
6	1	146	$C_{11}H_{14}$ methyltetralin	naphthenate
7	4	142	$C_{11}H_{10}$ methylnaphthalene	feel (some mothballs)

a. Approximate percentage of total 38-4 fraction.

FIGURE D-6 SILICONE PEAK 11 ON CARBOWAX

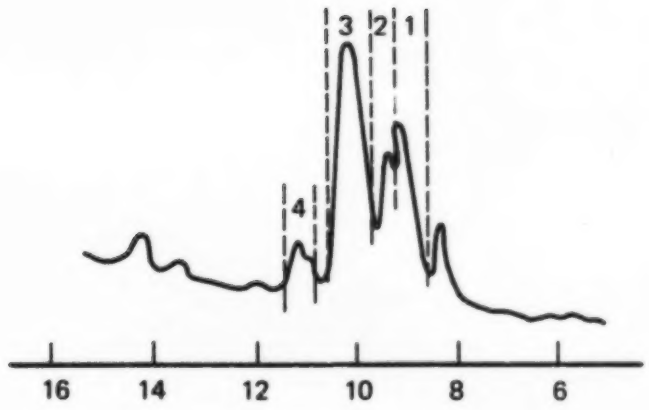


Carbowax Chromatogram
Temperature Program 100° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.5	174	$C_{13}H_{18}$ alkyl tetralin	irritation
2	1	160	$C_{12}H_{16}$ alkyl indan or tetralin	irritation
3	0.2		(not detected)	light kerosene
4	2	142	$C_{11}H_{10}$ methylnaphthalene	irritation

a. Approximate percentage of total 38-4 fraction.

FIGURE D-7 SILICONE PEAK 12 ON CARBOWAX

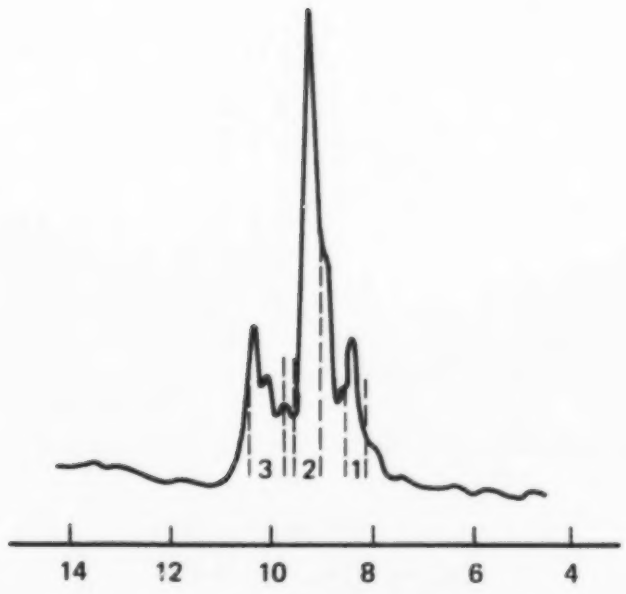


Carbowax Chromatogram
Temperature Program 150° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.2		(incomplete)	leathery
2	0.1		(incomplete)	oxidized oil
3	1	160	$C_{12}H_{16}$ alkyl indan or tetralin	heavy oil
	0.1	172	$C_{13}H_{16}$ alkyl indene	
4	0.05	158	$C_{12}H_{14}$ alkyl indene	heavy oil

a. Approximate percentage of total 38-4 fraction.

FIGURE D-8 SILICONE PEAK 13 ON CARBOWAX

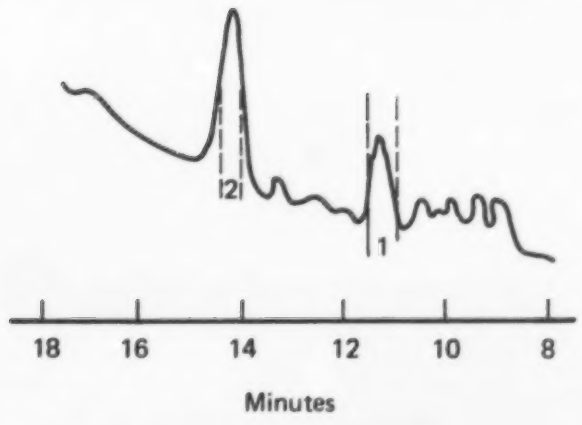


Carbowax Chromatogram
Temperature Program 150° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.2	–	incomplete, but probably alkyl benzene	oily
2	3	174	$C_{13}H_{18}$ alkyl indan or tetralin	linseed rubbery
		160	$C_{12}H_{16}$ dimethyltetralin	erasers (kerosene related)
3	0.2	160	$C_{12}H_{16}$ alkyl tetralin	kerosene

a. Approximate percentage of total 38-4 fraction.

FIGURE D-9 SILICONE PEAK 14 ON CARBOWAX

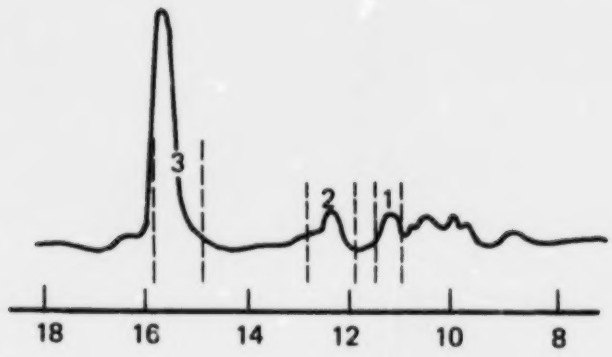


Carbowax Chromatogram
Temperature Program 150° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.1	160	$C_{12}H_{16}$ alkyl indan or tetralin	solventy (kerosene)
2	5	156	$C_{12}H_{12}$ dimethylnaphthalene	none
	0.01	162	$C_{10}H_{10}S$ dimethylbenzothiophene	

a. Approximate percentage of total 38-4 fraction.

FIGURE D-10 SILICONE PEAK 17 ON CARBOWAX

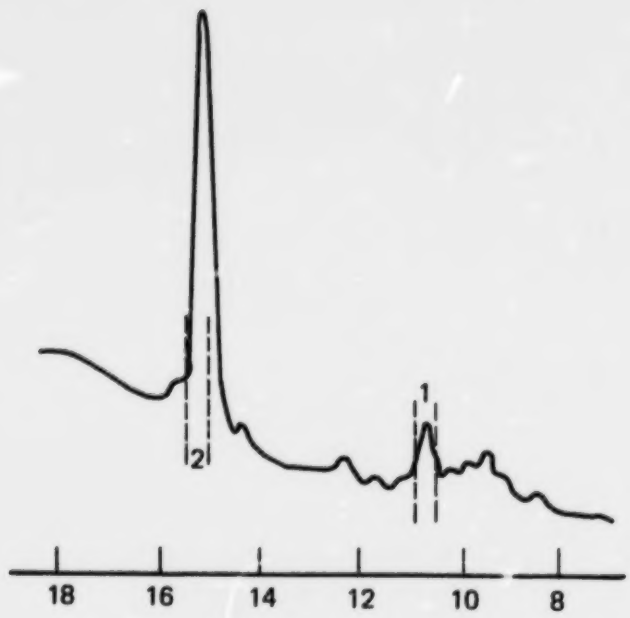


Carbowax Chromatogram
Temperature Program 150° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	0.1	174	$C_{13}H_{18}$ alkyl indan or tetralin	pungent, acrid
2	0.1	160	$C_{12}H_{16}$ alkyl indan or tetralin	kerosene
3	7	156	$C_{12}H_{12}$ dimethylnaphthalene	none

a. Approximate percentage of total 38-4 fraction.

FIGURE D-11 SILICONE PEAK 18 ON CARBOWAX



Carbowax Chromatogram
Temperature Program 150° to 200° at 4°C/min

CBW Peak	%[a]	MW	Composition	Odor
1	1	174	$C_{13}H_{18}$ $C_{12}H_{16}$ alkyl indans or tetralins	light kerosene
2	12	156	$C_{12}H_{12}$ dimethylnaphthalene	none
	0.5	168	$C_{13}H_{12}$ acenaphthene	
	0.01	162	$C_{10}H_{10}S$ dimethylbenzothiophene	

a. Approximate percentage of total 38-4 fraction.

FIGURE D-12 SILICONE PEAK 19 ON CARBOWAX

APPENDIX E

MASS SPECTROMETRY

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APPENDIX E

MASS SPECTROMETRY

1. PROCEDURE FOR COMPOUND IDENTIFICATION

Having isolated a gas chromatographic peak, high resolution mass spectral (HRMS) data was obtained for chemical identification of the compound.

Table E-1 is an example of the information obtained from the HRMS computer output for a single compound. The spectrum represents an alkyl indan or tetralin and was chosen for the sake of reporting simplicity. Typical outputs will range from five to fifty lines of mass-composition data. The output is basically a listing of data consisting of a series of high resolution mass peaks of varying intensity whose elemental composition can be calculated via mathematical consideration of how many combinations of elements can be found whose combined mass will equal that of the experimental mass. The mass spectral data provide a check on the degree of gas chromatographic separation of components and also enables us to identify multiple species when they are not resolved by the chromatographic steps.

The elemental composition determined from the HRMS data allows one to restrict the possible chemical structural choices for a particular compound to relatively few. In addition, the fragmentation patterns allow one to readily distinguish between choices such as an aromatic compound and an acyclic poly-olefin.

Details observed in the mass spectral pattern for the major chemical classes identified as being associated with the oily kerosene odor character are discussed below.

a. Benzenes

The range of alkyl benzenes observed includes C_3-C_5 alkyl substitution on the ring. It appears that most of the compounds are isomers with various combinations of methyl and ethyl substitution rather than a single alkyl group. The characteristic intense mass 91 (C_7H_7) ion observed in propyl, butyl and pentyl benzenes is weak in all of the spectra. In contrast, most of the alkyl benzenes have an intense peak for the parent molecule less a methyl group (M-15) consistent with fragmentation such as:

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TABLE E-1

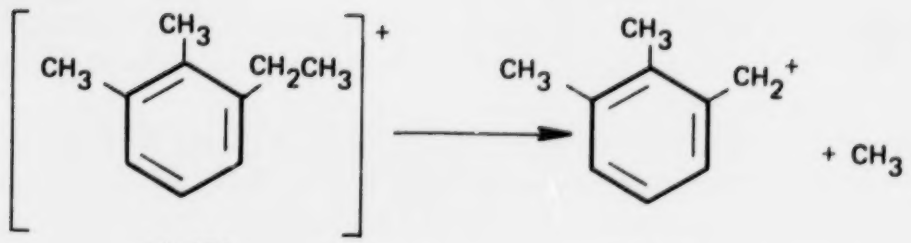
RESULTS OBTAINED FROM HIGH-RESOLUTION MASS SPECTROMETRIC STUDY ON SILICONE PEAK 11, CARBOWAX PEAK 3*

Mass	Intensity[a]	Elemental Composition			Possible Structure[b]
		Carbon	Hydrogen	Oxygen	
75.02615	2	6	3	0	
91.05527	2	7	7	0	$C_6H_5CH_2^+$
105.07106	1	8	9	0	
115.05483	3	9	7	0	
117.06929	1	9	9	0	
128.06207	2	10	8	0	
129.06982	2	10	9	0	
131.08538	3	10	11	0	
133.10158	2	10	13	0	
145.10141	6	11	13	0	$M - CH_3^+$
160.12471	3	12	16	0	trimethylindan (M^+)

a. Intensity on a scale of 1 to 10.

b. Deduced from chemistry and reference spectra.

*Experiment 38.

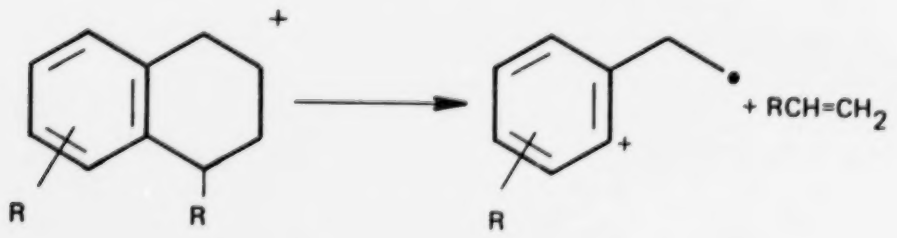


b. Naphthalenes

The naphthalenes studied contain either CH_3 or C_2H_5 substitution. There are two possible monomethylnaphthalene isomers, the 1- and 2-methyl derivatives, and both were observed. The C_2H_5 alkyl naphthalenes appear to be exclusively dimethyl derivatives, since none of them has the strong mass 141 ion expected of an ethyl derivative.

c. Indans and Tetralins (Benzocycloparaffins)

For the most part, it is very difficult to differentiate between the alkyl indans and the alkyl tetralins on the basis of their mass spectral fragmentation patterns. Each readily loses $\cdot CH_3$ and then a series of CH_2's. The tetralins may occasionally be identified by the characteristic loss of ethylene resulting in intense fragment ions at m/e 104, 118, etc.



(R may be H)

In those cases where the m/e 104 or 118 ions were intense, the compound was assigned the tetralin structure. Some fragmentation patterns seemed to be more consistent with the indan structure and were assigned accordingly. In other cases we were not able to choose between the two isomers.

2. SPECTRA INTERPRETATION

In addition to the guidelines for interpreting mass spectral data first reported in the 1969 Second Quarterly Report, it has been helpful in the interpretation of both the low-resolution and high-resolution data to expand on the fragment peak table reported by Gallegos *et al*[1] by including parent peaks and more compound types. The results of these calculations are reported in Tables E-2 to E-5.

The tables for the most part are self-explanatory, with the exception of the carbon number associated with each mass (peak). Each homologous series of partial or fragment peaks starts at a certain carbon number (shown in parentheses) and proceeds by the simple addition of a methylene unit. Thus, for the paraffins in Table E-2, mass 114 corresponds to C_8H_{18}, 128 corresponds to C_9H_{20}, and so forth. The mass 71 fragment ion in the same class corresponds to C_5H_{11}.

In Table E-3, the value in parentheses refers to the number of alkyl carbons attached to the basic nucleus. In this table, the zero indicates that the first mass in each of the parent ion listings corresponds to the unsubstituted nucleus. The significance of the parenthetical numbers is mixed in Table E-4, as explained in the footnotes. Because of the greater fragmentation pattern complexity, only parent ions are indicated in Table E-5.

These tables considerably speed the initial interpretation of mass spectral results while confirmatory high-resolution studies are in progress.

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1. E.J. Gallegos, J.W. Green, L.P. Lindeman, R.L. LeTourneau, and R.M. Teeter, *Anal. Chem., 39,* 1833 (1967).

TABLE E-2

PARENT AND FRAGMENT PEAKS USED IN MASS SPECTROMETRIC ANALYSIS PARAFFINS, OLEFINS AND BENZOPARAFFINS

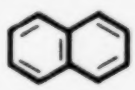
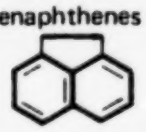
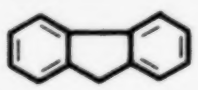
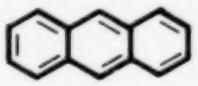
Compounds	Formula		Peaks[a]
Paraffins	C_nH_{2n+2}	Parents (8)[b]	114, 128, 142, 156, 170, 184, 198, 212
		Fragments (5)	71, 85, 99, 113, 127, 141, 155, 169
Monocycloparaffins Olefins[+]	C_nH_{2n}	Parents (8)	112, 126, 140, 154, 168, 182, 196, 210
		Fragments (5)	69, 83, 97, 111, 125, 139, 151, 165
Dicycloparaffins Dienes[+]	C_nH_{2n-2}	Parents (10)	138, 152, 166, 180, 194, 208, 222
		Fragments (8)	109, 123, 137, 151, 165, 179, 193, 207
Tricycloparaffins Trienes[+]	C_nH_{2n-4}	Parents (13)	178, 192, 206, 220, 234
		Fragments (11)	149, 163, 177, 191, 205, 219, 223, 247
Tetracycloparaffins	C_nH_{2n-6}	Parents (14)	190, 204, 218
		Fragments (12)	189, 203, 217
Benzocycloparaffins	C_nH_{2n-8}	Parents (9)	118, 132, 146, 160, 174, 188, 202, 216
		Fragments (9)	117, 131, 145, 159, 173, 187, 201
Benzodicycloparaffins	C_nH_{2n-10}	Parents (12)	158, 172, 186, 200
		Fragments (10)	129, 143, 157, 171, 185

a. High mass defect peaks.

b. Carbon number of first m/e value in series.

TABLE E-3

PARENT AND FRAGMENT PEAKS USED IN MASS SPECTROMETRIC ANALYSIS
ALKYL AROMATICS

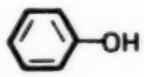
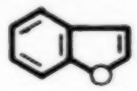
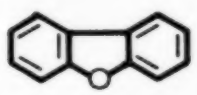
Compounds	Formula		Peaks[a]
Benzenes	C_nH_{2n-6}	Parents (0)[b]	78, 92, 106, 120, 134, 148, 162
		Fragments (1)	91, 105, 119, 133, 147, 151
Naphthalenes 	C_nH_{2n-12}	Parents (0)	128, 142, 156, 170, 184, 198, 212
		Fragments (1)	141, 155, 169, 183, 197
Acenaphthenes 	C_nH_{2n-14}	Parents (0)	154, 168, 182, 196, 210
		Fragments (1)	167, 181, 195, 209
Fluorenes 	C_nH_{2n-16}	Parents (0)	166, 180, 194, 208
		Fragments (0)	165, 179, 193, 207
Anthracenes 	C_nH_{2n-18}	Parents (0)	178, 192, 206, 220
		Fragments (1)	191, 205, 219

a. Low mass defect peaks (.094 mass less than paraffin).

b. Number of attached alkyl carbons for first m/e in series.

TABLE E-4

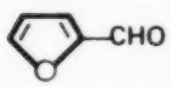
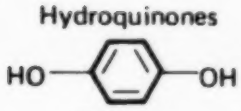
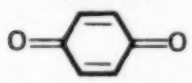
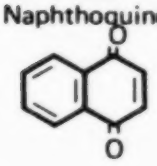
PARENT AND FRAGMENT PEAKS USED IN MASS SPECTROMETRIC ANALYSIS
MONO-OXYGENATED SPECIES

Compounds	Formula		Peaks
Alcohols + ethers	$C_nH_{2n+2}O$[a]	Parents (8)[c]	130, 144, 158, 172, 186, 200
		Fragments (7)[c]	115, 129, 143, 157, 171, 185, 199
Ketones + Aldehydes + Monocyclic ethers	$C_nH_{2n}O$[a]	Parents (8)[c]	128, 142, 156, 170, 184, 198
		Fragments (7)[c]	113, 127, 141, 155, 169, 183, 197
Monocyclic carbonyls + enones	$C_nH_{2n-2}O$[a]	Parents (8)[c]	126, 140, 154, 168, 182, 196
		Fragments (7)[c]	111, 125, 139, 153, 167, 181, 195
Dicyclic carbonyls + dienones	$C_nH_{2n-4}O$[a]	Parents (8)[c]	124, 138, 152, 166, 180, 194
		Fragments (7)[c]	109, 123, 137, 151, 165, 179, 193
Phenols 	$C_nH_{2n-6}O$[b]	Parents (0)[d]	94, 108, 122, 136, 150, 164
		Fragments (0)[d]	93, 107, 121, 135, 149, 163
Furans	$C_nH_{2n-4}O$[b]	Parents (0)[d]	68, 82, 96, 110, 124, 138
		Fragments (1)[d]	81, 95, 109, 123, 137
Benzofurans 	$C_nH_{2n-10}O$[b]	Parents (0)[d]	118, 132, 146, 160, 174, 188, 202
		Fragments (1)[d]	131, 145, 159, 173, 187, 201
Dibenzofurans 	$C_nH_{2n-16}O$[b]	Parents (0)[d]	168, 182, 196, 210
		Fragments (1)[d]	181, 195, 209

a. High mass-defect peaks.
b. Low mass-defect peaks.
c. Number of carbon atoms.
d. Number of attached alkyl carbons starting m/e series.

TABLE E-5

PARENT PEAKS USED IN MASS SPECTROMETRIC ANALYSIS
DIOXYGENATED SPECIES

Compounds	Formula		Parent Peaks[a]
Aliphatic acids RCOOH	$C_nH_{2n}O_2$	(4)[b]	88, 102, 116, 130, 144, 158
Monocyclic or unsaturated acids	$C_nH_{2n-2}O_2$	(6)[b]	114, 128, 142, 156, 170
Furfurals  and	$C_nH_{2n-6}O_2$	(0)[c]	96, 110, 124, 138
Hydroquinones 	$C_nH_{2n-6}O_2$	(0)[c]	110, 124, 138
Quinones 	$C_nH_{2n-8}O_2$	(0)[c]	108, 122, 136, 150
Naphthoquinones 	$C_nH_{2n-14}O_2$	(0)[c]	158, 172, 184

a. Fragmentation patterns complicated.

b. Starting carbon number.

c. Number of attached alkyl carbons starting series.

APPENDIX F

COMPARISON OF YEAR 1 AND YEAR 2 DIESEL FUEL

APPENDIX F

COMPARISON OF YEAR 1 AND YEAR 2 DIESEL FUEL

A new 2000-gallon supply of diesel fuel was obtained, as before, from the Mobil New Haven depot.

A sample of the fuel was submitted to F. Hills for routine analysis; a comparison summary of the results obtained for the Year 1 and 2 fuels is given in Table F-1. The most notable difference in the fuels is a small (about 20°F) shift to a higher boiling range for the new fuel.

The gas chromatogram of the new fuel is shown in Figure F-1 and that of the old fuel in Figure F-2. These chromatograms reveal a slight increase in mean molecular weight for the new fuel, as evidenced by slightly less C_{10} and somewhat more C_{15} hydrocarbons, consistent with the Mobil analysis.

The odor of the new fuel in the test room is basically similar to that of the original fuel, except that the kerosene note in the new supply is sharper and more like Stoddard solvent. In addition, a slight tarry naphthenate odor is perceived.

Diesel exhaust using the new fuel has been studied at three levels – 2, 20 and 60 liters – in the odor test room. The basic odor is about the same as before, although the smoky-burnt odor is somewhat more tarry. An acrid character is also observed that is somewhat similar to the choking quality of larger amounts of the original fuel exhaust.

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TABLE F-1

INSPECTIONS OF CAPE 7 – A.D. LITTLE TEST FUEL

	Year 1	Year 2
Sample No.	68-38632	69-44233
Gravity, °API D287	40.4	38.7
ASTM Distillation, °F D86		
Initial	350	364
10%	378	396
50%	418	436
90%	466	497
End Point	495	524
Flash Point, °F D93	136	154
Aniline Point, °F D97-2	135.0	135.0
Sulfur, Wt. %	0.18	0.19
Mercaptan Sulfur – Total, ppm	< 0.5	< 0.5
Mercaptan Sulfur – NaOH Extract, ppm	< 0.5	< 0.5
Disulfide Sulfur, ppm Volatile	429	237
Non-Volatile	356	389
Phenol, ppm	133	177
Thiophenol, ppm	2	3.2
Conjugated Dienes, Millimole/gm	6.9	
Bromine No. D1159	0.6	0.7
Fluorescent Indicator Adsorption D1319		
Aromatics, % Vol	17.7	20.8
Olefins, % Vol	1.4	2.8
Saturates, % Vol	80.9	76.4
Nitrogen, ppm	3.3	
Cetane No. D613	45.9	
Cetane Index (calculated)	44.0	44.0
Ash, % D482	< 0.001	< 0.001
Copper Strip Corrosion D1130	2A	1B
Viscosity @ 100°F, cs D445-3	1.56	1.76
Color D1500	L 0.5	L 0.5

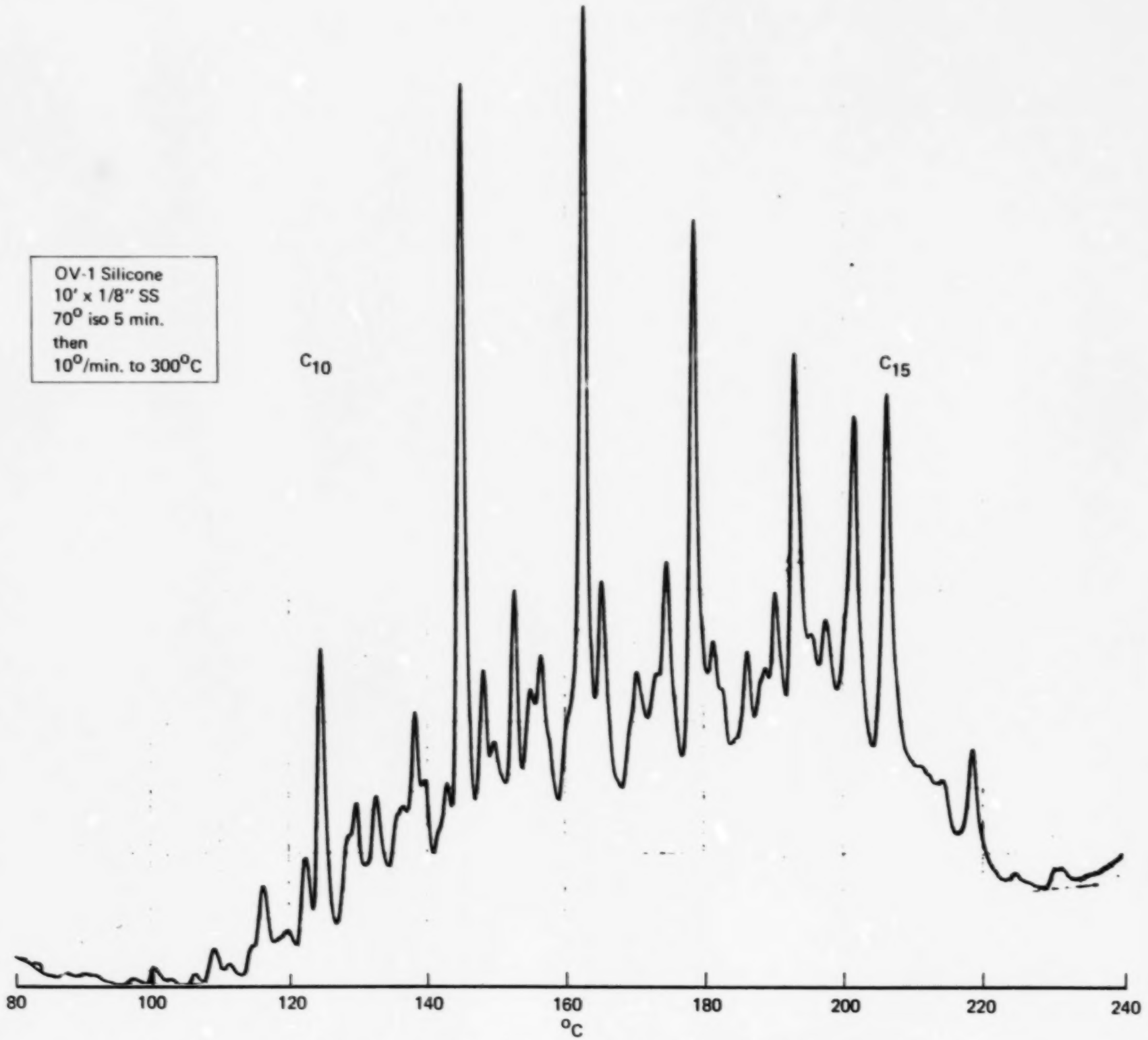

FIGURE F–1 SILICONE GAS CHROMATOGRAM OF NEW FUEL

OV – 1 Silicone
10' x 1/8" SS
70° iso 5 min.
then
10°/min to 300°C

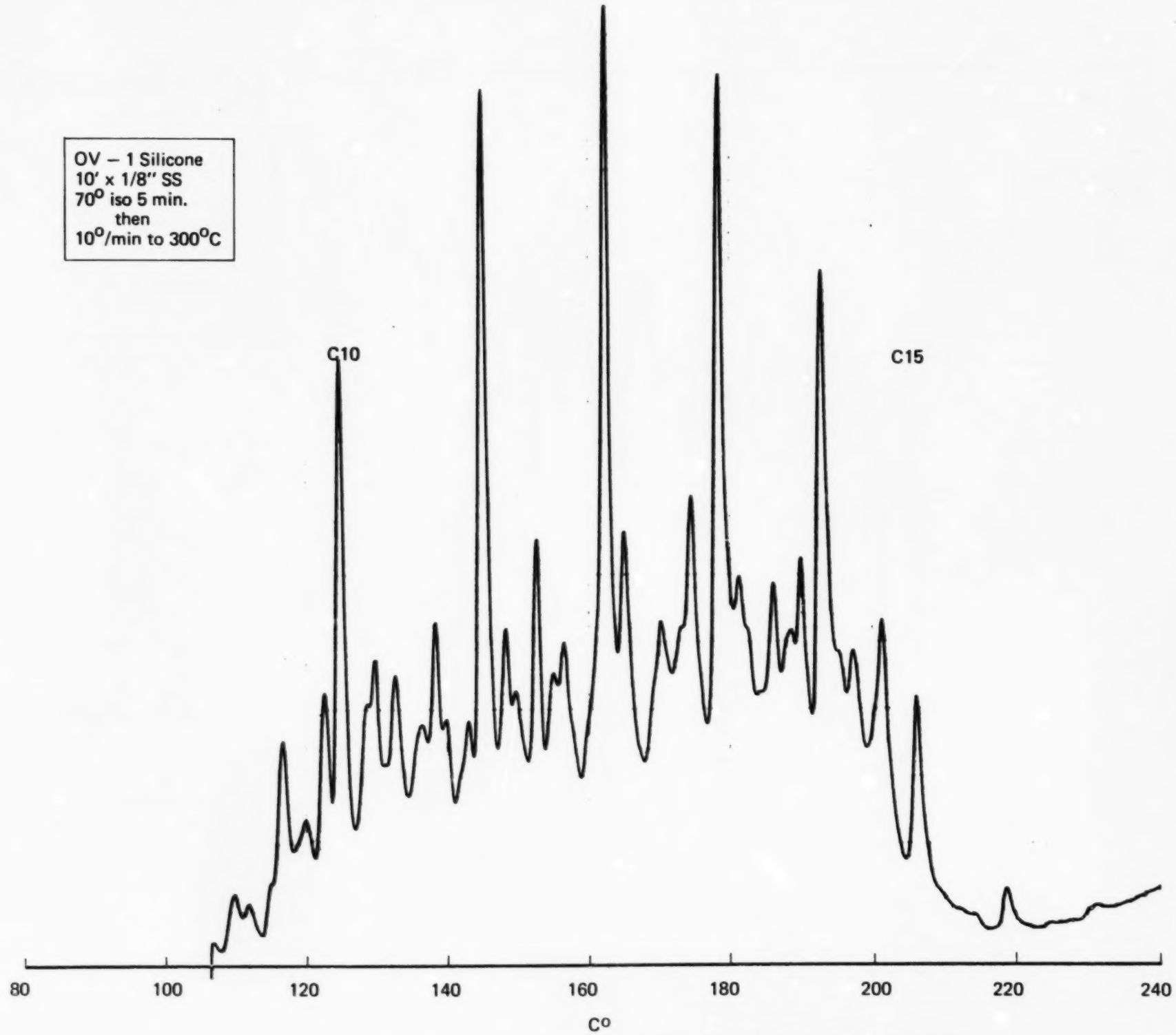

FIGURE F - 2 SILICONE GAS CHROMATOGRAM OF OLD FUEL

APPENDIX G

EFFECTS OF CHEMICAL TREATMENT ON EXHAUST AND FUEL ODOR

APPENDIX G

EFFECTS OF CHEMICAL TREATMENT ON EXHAUST AND FUEL ODOR

1. EFFECT OF pH ON THE SMOKY-BURNT ODOR COMPLEX

We attempted a few experiments with the standard SiO_2-10 smoky-burnt fraction to see whether we could resolve the odors of interest in a manner which would be more suitable for GC separation. We attempted to extract an ether solution of the smoky-burnt odor complex both by a sequence involving hydrochloric acid, sodium bicarbonate, sodium hydroxide, and Girard T and by a set of parallel experiments using these reagents on smaller aliquots of the total sample.

The experiments and their results are summarized in Figure G-1 and Table G-1. Examination of the infrared spectra of the various fractions indicates that one indeed obtains a chemical separation, but the smoky-burnt odor complex obviously cannot withstand these extremes of pH without chemical decomposition. The fact that the aqueous condensate itself has a pH of 2.3-2.5 suggests that we may obtain more odor by buffering the condensate-receiving flasks.

It is certain from these experiments and from what others have found that one has to be careful with sample handling conditions, especially as the odor complexes are obtained in increasingly concentrated stages.

2. EFFECT OF CHEMICAL TREATMENT ON THE FUEL ODOR

In an effort to gain some insight into the chemical nature of the components responsible for the odor of fuel oil, we mixed 20 ml of fuel oil with an equal volume of various reagents in a separatory funnel. The treated oil was then washed three times with distilled water to remove the reagent. The oil was then smelled; where possible, so was the spent reagent. Reagents used and their effect on the fuel oil odor were as follows:

HCl (1N) – No observable change in fuel oil odor; the spent HCl phase did not appear to have a naphthenate-related odor.

NaOH (1N) – Caustic appears to flatten out and decrease the total odor, possibly the oily-sour component.

Nitric Acid (1N) – The treated fuel oil appeared to have a higher intensity of burnt, kerosene, and tarry notes than a comparable control. Exhaustive treatment of fuel oil with concentrated nitric acid removes all these character notes, leaving an oily-sweet odor.

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Nitric Acid (1N) – The odor of the treated fuel oil is primarily sweet (fennel or cinnamaldehyde-related ?) and the kerosene note has an increased Stoddard solvent or top-note character. The spent nitrous acid has an earthy-related odor.

Stannous Chloride (SAT) – Decreases the oily-kerosene intensity and increases the burnt-tarry character. Continued contact of the oil with stannous chloride produced a sulfide odor.

Ascorbic Acid – No apparent effect on the odor of the fuel oil.

Furfural – Fuel oil treated with furfural has a distinct odor of drying oil (linseed) and a musty character.

Experiments of this type may prove useful in determining the species responsible for the odor and in devising methods for modifying the odor.

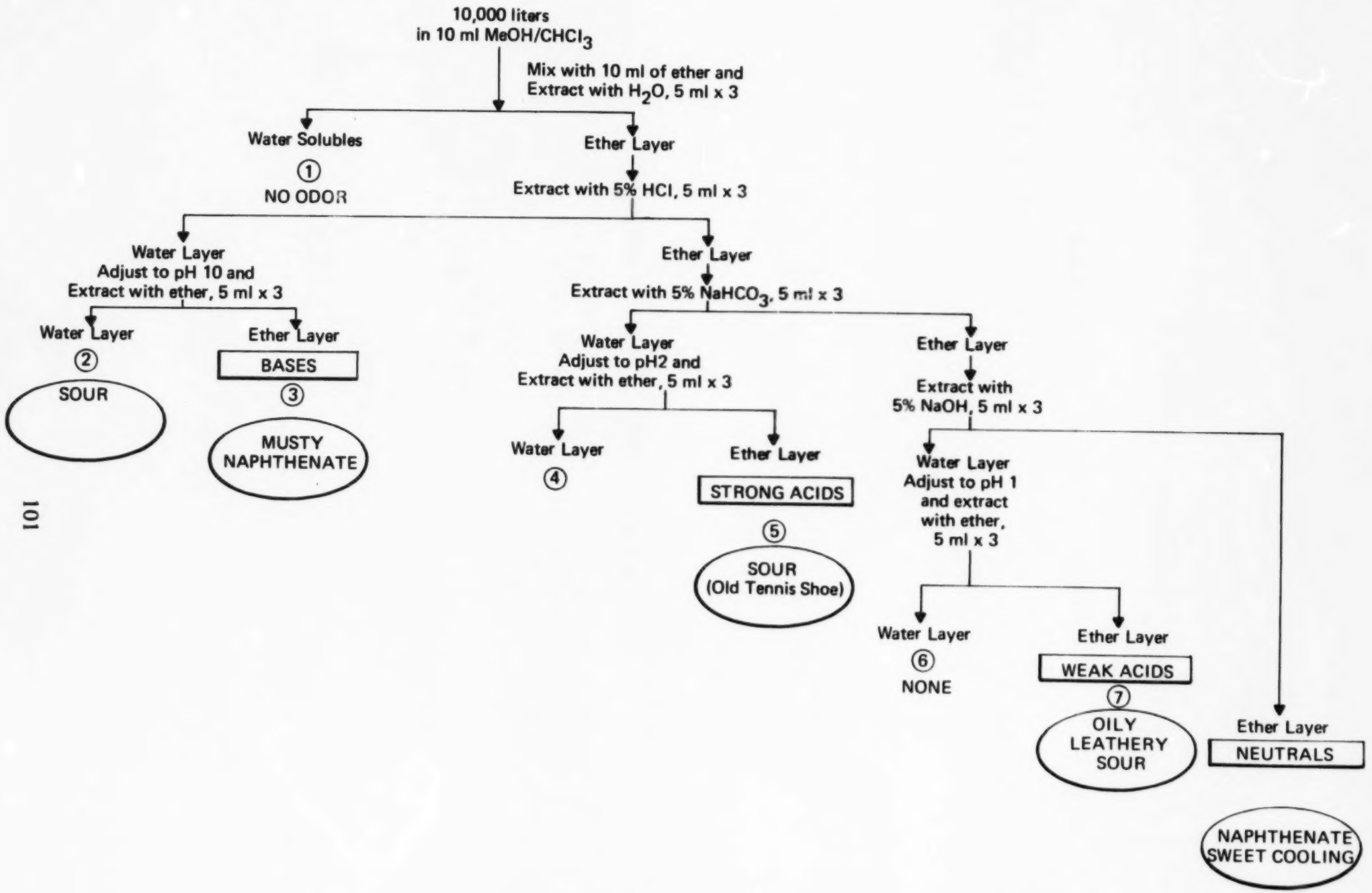

FIGURE G–1 pH SEQUENTIAL EXTRACTION OF 10,000 ℓ OF CONDENSATE SiO_2 –10

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TABLE G-1

CONDENSATE 30 SiO_2-10 PARALLEL EXTRACTION[a]

Extractant		Phase	Sample	Odor (blotter strip)
SiO_2-10 (Et_2O)	H_2O	Ether	B	SB[b], naph., sour leathery
		Aq.	A	Slight musty
SiO_2-10 (Et_2O)	HCl	Ether	D	SB, oily sour
		Aq. (regen)	C-1	Slight sour oily
SiO_2-10(Et_2O)	$NaHCO_3$	Ether	F	SB, oily leather
		Aq. (regen)	E-1	Fatty acid sour
SiO_2-10 (Et_2O)	NaOH	Ether	H	Weak earthy musty
		Aq. (regen)	G-1	Woody musty, oily, phenolic
SiO_2 - 10 (Et_2O)	Girard T	Ether	J	Sour[c]
		Aq. (regen)	K	Sour oily

a. 2000 ℓ aliquots.

b. Smoky-burnt.

c. May have had SB carbonyls which were oxidized on handling.

APPENDIX H

EXAMINATION OF EXHAUST CONDENSATE FROM A HEPTANE-FUELED ENGINE

APPENDIX H

EXAMINATION OF EXHAUST CONDENSATE FROM A HEPTANE-FUELED ENGINE

The condensate from a 6V-71 diesel running on heptane fuel was obtained by Mr. Joseph Colucci of General Motors and sent to us for a comparative analysis. We received approximately 3.2 liters of the aqueous condensate, which corresponds to about 200,000 liters of exhaust in our experiments using normal diesel fuel.

The condensate was extracted in the usual manner with pentane and chloroform. The concentrated extracts were then submitted to the standard silica gel LCC elution scheme whereby 12 fractions were obtained. The odor of each of the fractions was determined by blotter strip methods. GC profiles were obtained on the SiO_2–1, -5, and -10 fractions.

In our third quarterly report (November 20, 1968) we reported our odor observations on a single-cylinder diesel engine which was fueled with heptane. The odor descriptions of the exhaust were:

Sour, oxidized oily	1½
Burnt waxy	1

The smoky-burnt and kerosene odors characteristic of diesel engine exhaust were not observed. The odors observed on the LCC column fractions are listed in Table H-1.

TABLE H-1

LCC SAMPLES FROM HEPTANE EXHAUST

Fraction	Eluting Solvent	Odor
1	Pentane	No odor
2	Pentane	No odor
3	Pentane	No odor
4*	Benzene	Leathery sour, rubbery sulfide
5	Benzene	Green ?
6	Benzene	No odor
7	$CHCl_3$	Phenolic ?
8	MeOH/$CHCl_3$	Oily ?
9	MeOH/$CHCl_3$	Papery
10*	MeOH/$CHCl_3$	Burnt charred sweet
11	MeOH/$CHCl_3$	Rancid citral
12	MeOH	Rancid citral

*Highest intensity of odor.

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The intensities overall were low, with fractions 4 and 10 having the highest intensity. In the normal diesel fuel samples, fractions 1-3 do not contain odor, fractions 4 and 5 contain the oily-kerosene odor, and fraction 10 contains the smoky-burnt odor.

One of the more interesting comparisons of the samples comes in their GC profiles, as shown in Figures H-1 and H-2 of fractions 1 and 10. Fraction 5 did not contain sufficient material to give a GC elution pattern. In SiO_2-1 (Figure H-1), the hydrocarbon fraction, nothing begins to elute for 12 minutes at 190°C and most of the material elutes between 230° and 280° C. These higher temperatures probably correspond to hydrocarbons boiling in the $C_{14}-C_{20}$ range. Under these conditions, heptane elutes in 1.5 minutes at 100°C. The complete absence of intermediate hydrocarbons is probably more indicative of the losses incurred in the sample trapping and handling procedures, but the observation of the abundant higher hydrocarbons certainly speaks for the complicated chemistry which occurs in the diesel engine.

The profile of the burnt fraction (SiO_2-10, Figure H-2) generally elutes over a lower temperature range than the hydrocarbon fraction and is less complicated in appearance than is normal for the comparable fraction from the exhaust of our diesel-fueled engine.

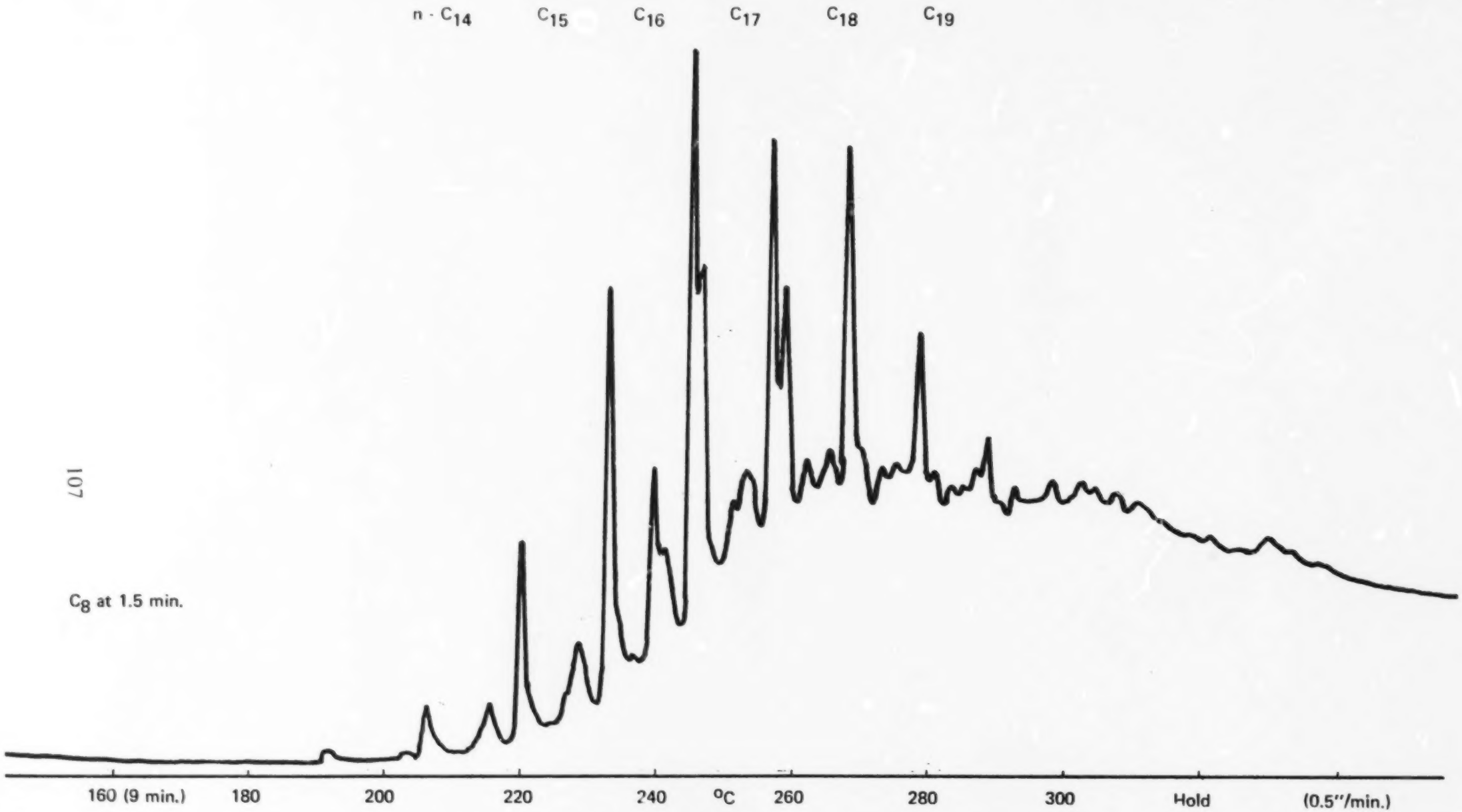

FIGURE H–1 HEPTANE EXHAUST LCC SiO_2-1 FRACTION (Hydrocarbons)

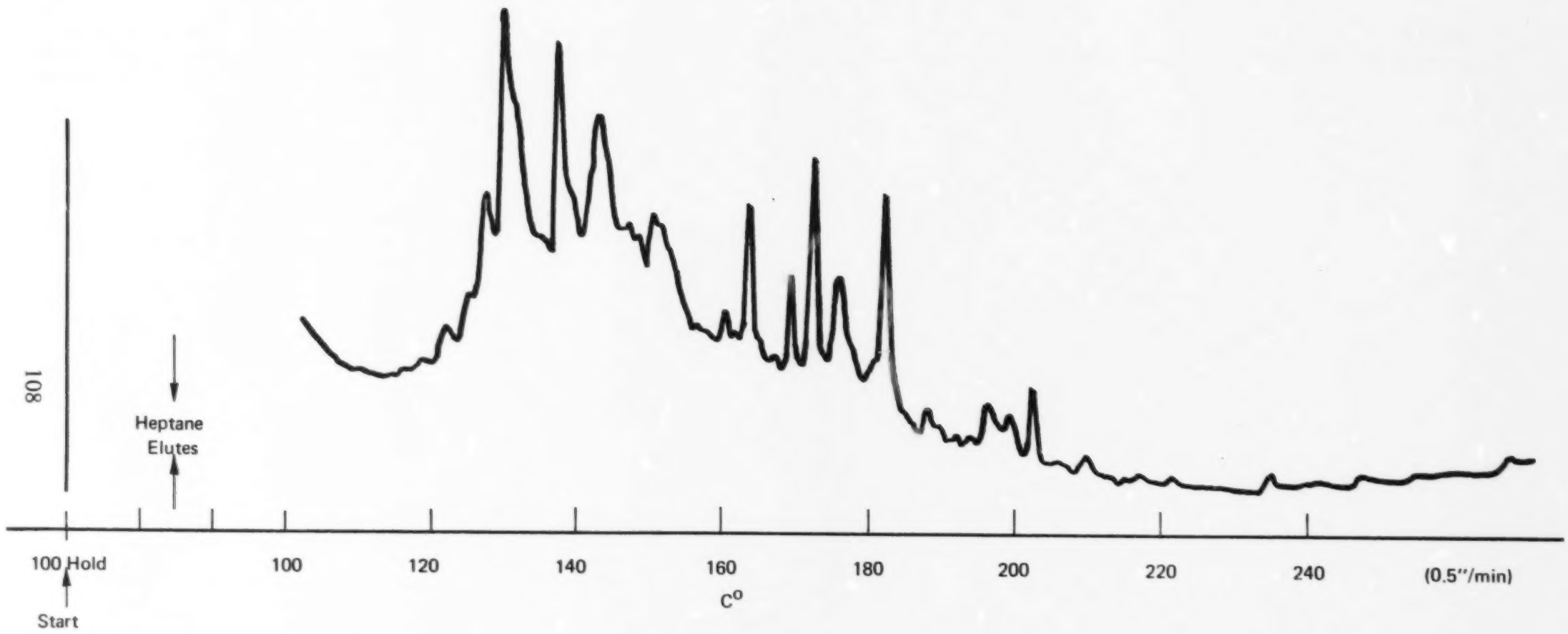

FIGURE H - 2 HEPTANE EXHAUST LCC SiO_2 - 10 FRACTION (BURNT)

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APPENDIX I

GEL PERMEATION CHROMATOGRAPHY

APPENDIX I

GEL PERMEATION CHROMATOGRAPHY

The use of gel permeation chromatography as a second-stage separation method for the smoky-burnt odor complex obtained from the silica gel column affords a different means of resolving the sample than the adsorption methods which we have been studying. Since the method separates on the basis of molecular size, it is attractive as a way to obtain well separated fractions for subsequent gas chromatographic resolution.

Although this technique has been used primarily for studies on polymers, researchers at Waters Associates (Framingham, Massachusetts) have recently published a report on the resolution of samples in the 80-200 molecular weight range on a newly developed gel medium.[1] During this last quarter, therefore, we arranged with Waters Associates to run several samples to test the potential of the method. At present we have studied only a single, small sample, but the results are encouraging. A 1000-liter aliquot of smoky-burnt 42-10 was chromatographed on 15 feet of Styragel using chloroform as a solvent. Figure I-1 is the chromatogram of the 14 eluting fractions as indicated by a refractive index monitor. Both negative and positive peaks are obtained, since this detector compares the refractive index of the eluant to pure solvent. Blotter-strip evaluation of the collected fractions indicates that smoky-burnt related odors are present in fractions 5, 6, and 7.

Studies on a 5000-liter sample from fraction 43-10 were hindered by problems of sample instability and solvent impurities and no useful results were obtained from the sample. Nevertheless, the method is attractive, because the separation is based on a new molecular property and it may find utility in later studies.

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1. K.J. Bombaugh, W.A. Dark and R.F. Lavangie, *Separation Science, 3,* 375 (1968).

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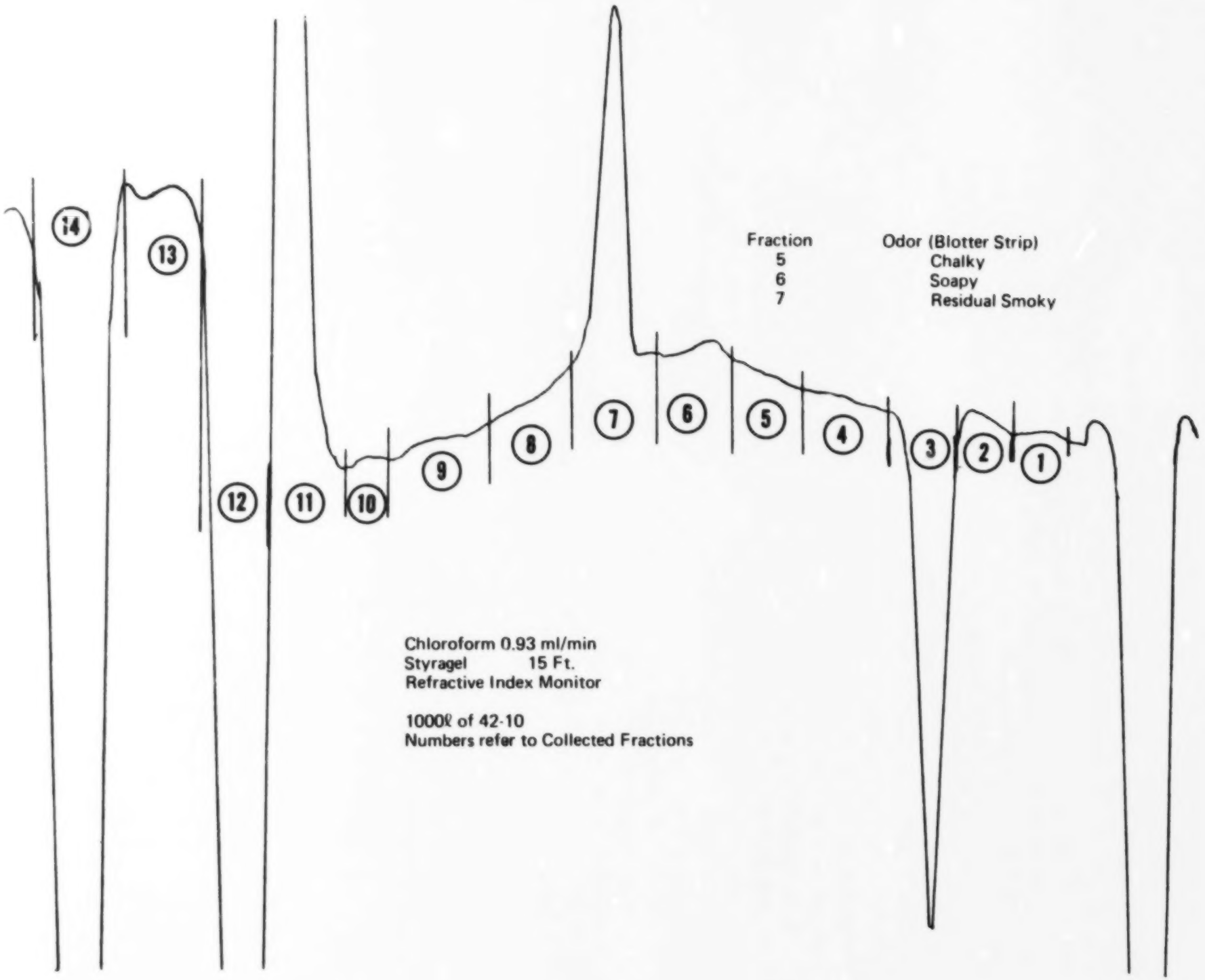

FIGURE I-1 GEL PERMEATION CHROMATOGRAM OF 42-10 SMOKY-BURNT FRACTION